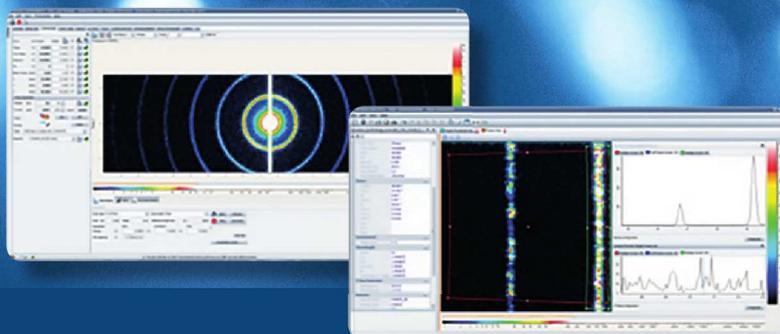


**14th European Powder Diffraction Conference
Aarhus, 15-18 June 2014**

EPDIC14

BOOK OF ABSTRACTS

LYNXEYE XE: Energy dispersive 0D/1D/2D mode



The 1st and only detector on the market enabling energy dispersive zero-, one- and two-dimensional diffraction

- Superb energy resolution making K β filters, mirrors and secondary monochromators redundant
→ Unrivalled filtering of sample fluorescence
- Operation with all common characteristic X-ray emission lines (Cr, Co, Cu, Mo, and Ag radiation)
- Variable sample to detector distance to optimize 2θ - and γ -coverage
- No defective strips at delivery time - guaranteed
- Full integration in DIFFRAC.SUITE

Innovation with Integrity

XRD

The new "Dynamic Beam Optimization" concept



Superior suppression of instrument background, specifically of air scatter at low angles 2θ

- Motorized Anti Scatter Knife: Fully software controlled retraction of the knife to prevent any cropping of the beam
 - Fully compatible with both the Bragg-Brentano geometry (fixed as well as variable divergence slits) and the parallel beam geometry
- Variable Active Detector Window: Fully software controlled switching on of individual strips to open the detector window as a function of 2θ
- Acquisition of diffraction data with virtually no instrument background starting at angles as low as about $0.2^\circ 2\theta$
- Full integration in DIFFRAC.SUITE

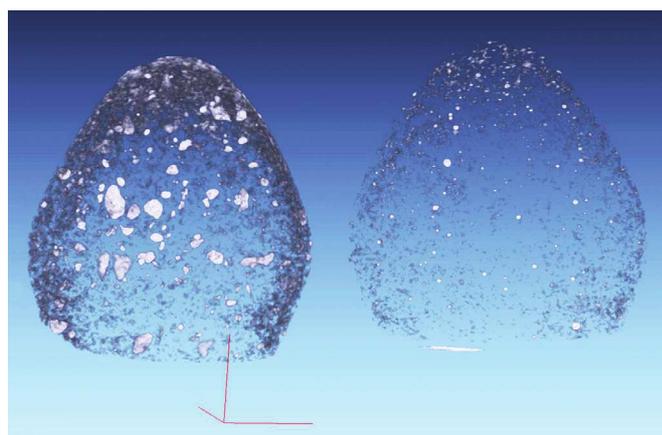
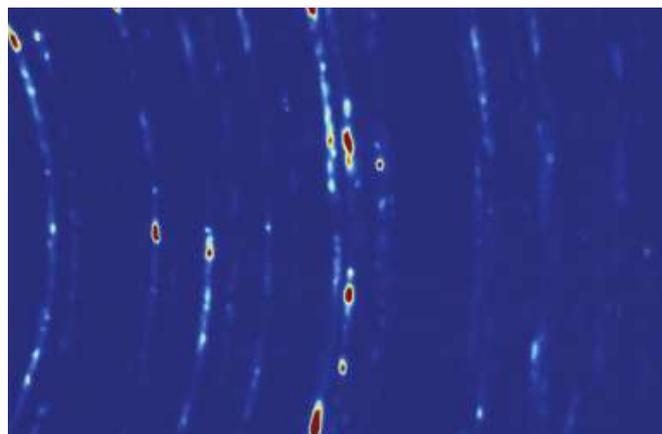
www.bruker.com

Innovation with Integrity

XRD

EMPYREAN

The multipurpose solution to your analytical needs



The only XRD platform that does it all

- Powders
- Thin films
- Nanomaterials
- Solid objects

With the Empyrean, PANalytical has set the new standard for a multipurpose diffractometer.

Empyrean not only meets the high expectations of scientists and XRD experts today, but will continue to do so as research themes evolve.



For more information please contact us at:

info@panalytical.com
www.panalytical.com

Cutting-edge technology. Ultimate commitment.



PANalytical
get insight

BETTER MEASUREMENTS.
BETTER CONFIDENCE.
BETTER WORLD.

0D, 1D and 2D all from a single detector



Introducing Rigaku's new HyPix-3000

- Ultra-high dynamic range and high sensitivity
- Seamless switching from 2D-TDI mode to 2D snapshot mode to 1D-TDI mode to 0D mode with a single detector
- XRF suppression by high and low energy discrimination
- High spatial resolution, direct-detection pixel array detector



DECTRIS®

detecting the future

MYTHEN PRODUCT FAMILY

MYTHEN X-ray detector systems have transformed data acquisition at synchrotron beamlines and laboratory X-ray sources. Their key benefits include superior data quality, fast data acquisition and simple, maintenance-free operation.

- Fluorescence suppression
- Radiaton-tolerant design
- Electronic gating and external trigger
- Shutterless operation
- Maintenance-free operation



laboratory, industry and synchrotron

sales@dectris.com | www.dectris.com

Make the SMART move to PDF-4+

ICDD databases are the only crystallographic databases in the world with quality marks and quality review processes that are ISO certified.

Standardized data

More coverage

All data sets are evaluated for quality

Reviewed, edited and corrected prior to publication

Targeted for material identification and characterization

PDF-4+ 2013 features 340,653 entries
including 227,102 entries with atomic coordinates.

Visit our booth at EPDIC



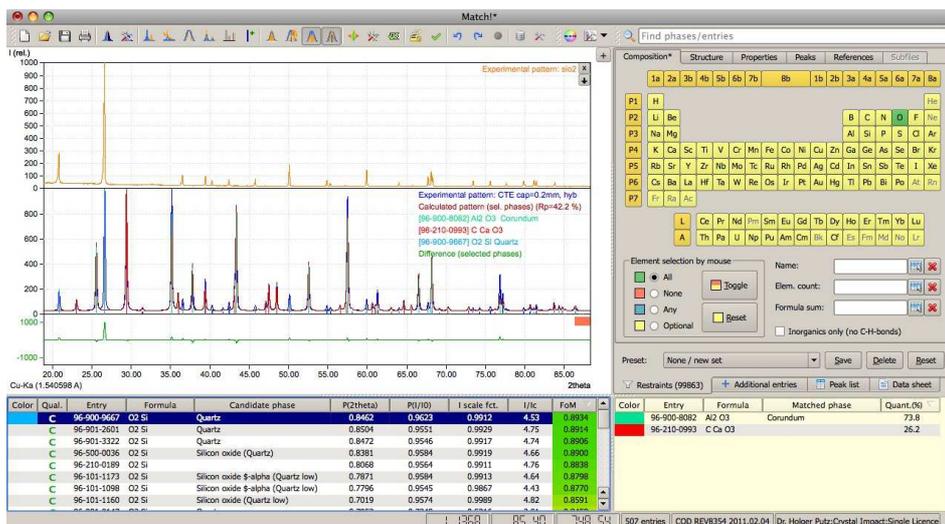
www.icdd.com | marketing@icdd.com
610.325.9814 | toll-free 866.378.9331
(U.S. & Canada)



ICDD, the ICDD logo and PDF are registered in the U.S. Patent and Trademark Office.
Powder Diffraction File is a registered trademark of JCPDS-International Centre for Diffraction Data.
©2014 JCPDS-International Centre for Diffraction Data.

MATCH!

Phase Identification from Powder Diffraction - Version 2



More features:

- ✓ Fast multiple phase identification
- ✓ Stacked display of multiple exp. patterns
- ✓ Perpetual restraining database retrieval
- ✓ Convenient editing of peaks and background modification using the mouse

System requirements:

- ✓ Windows XP, Vista, Windows 7 or 8; Mac OS X 10.5.8 "Leopard" or higher; Linux (Intel 32-bit), e.g. openSUSE, Ubuntu, Fedora
- ✓ 1 GB of RAM
- ✓ 1.5 GB of free disc space

Match! is an easy-to-use software for phase identification from powder diffraction data. It compares your diffraction pattern to a database containing reference patterns, in order to identify the phases present in your sample.

Additional knowledge about the sample like known phases, elements or density can be applied easily. In addition to this **qualitative analysis**, a **quantitative analysis** (using Rietveld refinement) can be performed as well.

As reference database, you can apply the included free-of-charge COD database, any ICDD PDF product, and/or create a user database based on your own diffraction patterns or crystal structure data.

Match! also provides a gentle introduction into **Rietveld refinement**, using the well-known FullProf package (by J. Rodriguez-Carvajal) in the background.

You can download a full-featured demo version free-of-charge:

<http://www.crystalimpact.com/match>

Diamond, the well-known program for the visualization and exploration of crystal structures, has been improved again: The upcoming version 4 contains a lot of new features, in addition to many functions that have been enhanced significantly:



DIAMOND

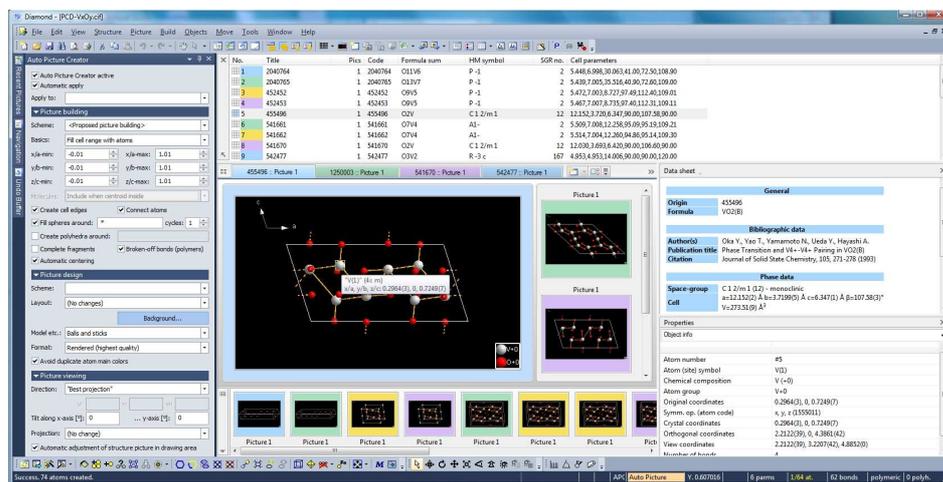
Crystal and Molecular Structure Visualization

Checkout the new **Auto Picture Creator** on the left-hand side that automatically applies changes in building options, design and viewing direction directly to the structure picture.

Use the new mode for a much more **intuitive exploration of crystal or molecular structures**, and to **pre-view neighbouring atoms and molecules**. Benefit from the improved evaluation of bonding spheres, or let Diamond determine atom site environments automatically basing upon **Dirichlet domains** (Voronoi polyhedra).

You can **download the full-featured Diamond 4 beta version free-of-charge** from:

<http://www.crystalimpact.com/diamond/v4download.htm>



More new features:

- ✓ Intuitive structure exploration using the mouse wheel
- ✓ Apply user-defined design schemes
- ✓ Retrieve and get crystal structure data from the COD (Crystallography Open Database)

System requirements:

- ✓ Windows XP, Vista, Windows 7 or 8
- ✓ Microsoft Internet Explorer 5.01 (or higher)
- ✓ 512 MB of RAM (or more)
- ✓ 5 GB of free disc space



Tel.: +49 (228) 981 36 43
Fax: +49 (228) 981 36 44
E-mail: info@crystalimpact.com
<http://www.crystalimpact.com>

CRYSTAL IMPACT GbR
Kreuzherrenstr. 102
53227 Bonn
Germany

Born to find out



Anton Paar

Non-ambient Attachments for X-Ray Diffraction

- ▶ Innovative designs dedicated to our customers' needs
- ▶ Unmatched robustness and reliability for long-term use
- ▶ Compact and easy to use



www.anton-paar.com

EPDIC14 – Book of Abstracts

14th European Powder Diffraction Conference

Aarhus, 15-18 June 2014

*Aarhus University
Denmark*

Table of contents

<i>Committees</i>	<i>iii</i>
<i>Foreword from EPDIC14 Chairman</i>	<i>vii</i>
<i>Program Overview</i>	<i>xi</i>
<i>Opening Lecture:</i>	<i>1</i>
<i>Honorary Lectures:</i>	<i>5</i>
<i>Plenary Lectures</i>	<i>9</i>
<i>Microsymposium MS01: Total Scattering Techniques and Disorder</i>	<i>15</i>
<i>Microsymposium MS02: Ab initio Structure Solutions</i>	<i>33</i>
<i>Microsymposium MS03: Biological and Molecular Materials</i>	<i>43</i>
<i>Microsymposium MS04: Combined Methods for Structure Analysis:</i> <i>Electron diffraction, Powder diffraction & Tomography</i>	<i>51</i>
<i>Microsymposium MS05: Energy Materials</i>	<i>61</i>
<i>Microsymposium MS06: Progress in instrumentation</i>	<i>77</i>
<i>Microsymposium MS07: Diffraction line profile analysis, stress,</i> <i>strain and texture</i>	<i>89</i>
<i>Microsymposium MS08: In situ, in operando studies</i>	<i>103</i>
<i>Microsymposium MS09: Nanomaterials, surfaces and interfaces</i>	<i>125</i>
<i>Microsymposium MS10: Neutron Structural and Magnetic Scattering</i>	<i>137</i>
<i>Microsymposium MS11: Structure and properties of functional</i> <i>materials</i>	<i>143</i>
<i>Microsymposium MS12: Diffraction under pressure</i>	<i>169</i>
<i>Authors Index</i>	<i>179</i>

Committees

EPDIC Scientific Committee:

N. Audebrand, Rennes, France
P. Bordet, Grenoble, France
M. Brunelli, Grenoble, France
R.J. Cernik, SRS, Daresbury, UK - Vice-Chairman
R. Cerný, Genève, Switzerland
W.I.F. David, ISIS, Oxford, UK
S. Eriksson, Göteborg, Sweden
A.N. Fitch, ESRF, Grenoble, France
M. Fransen, PANalytical, Almelo, The Netherlands
H. Fuess, Darmstadt, Germany
A. Goodwin, Oxford, UK
A. Guagliardi, Bari, Italy
J.-E. Jørgensen, Aarhus, Denmark
A. Kern, Bruker AXS, Karlsruhe, Germany
A. Kremenovic, Belgrade, Serbia
R. Kuzel, Prague, Czech Republic
I. Margiolaki, Grenoble, France
B. Palosz, UNIPRESS, Warsaw, Poland
D. Rafaja, Freiberg, Germany
J. Rius, Barcelona, Spain
P. Scardi, Trento, Italy - Chairman
P. Whitfield, Ottawa, Canada

EPDIC14 Local Organising Scientific Committee:

Jens-Erik Jørgensen, AU – Chairman
Torben R. Jensen, AU
Henrik Birkedal, AU
Mogens Christensen, AU
Bo Brummerstedt Iversen, AU

Conference secretaries

Marianne Sommer Immersen, AU
Charlotte Rud Nielsen, AU

Foreword from EPDIC14 Chairman

Jens-Erik Jørgensen, Aarhus University, Denmark

Dear colleagues,

The local organizing committee is very pleased to welcome all participants of the 14th European Powder Diffraction Conference held at Aarhus University 15-18 June 2014 and we are very happy that the city of Aarhus has been chosen to host EPDIC 14.

The EPDIC conferences started in 1991 and have since then been the natural reference point for presentation of scientific results and new developments within the field of powder diffraction. This is reflected in the scientific program of EPDIC 14, which covers a broad spectrum of topics ranging from methods for structural and microstructural investigation of powders to ab initio solution methods and studies of biological and molecular materials. A substantial part of the program is dedicated to topics such as total scattering techniques, studies of structure and properties of functional and energy material. Diffraction studies under non-ambient conditions have in recent years gained importance, which is reflected in the program by sessions on diffraction under pressure and in situ, in operando studies. In addition to the scientific sessions, commercial exhibitions will also take place during the meeting allowing companies to present new products related to powder diffraction.

We hope that EPDIC 14 will give scientists of all generation the opportunity to exchange ideas and views, and special effort has been given to provide grants for young scientists to enable them to participate in the conference.

It is our hope that the participants will have a scientifically interesting meeting and an enjoyable stay in Aarhus.

Jens-Erik Jørgensen

Chairman of EPDIC 14

Program Overview

Monday 16 June 2014 Morning		Monday 16 June 2014 Morning	
8h30	<p>Plenary Lecture: Lakeside Theaters, Chair: Thomas Hansen</p> <p><i>Microstrain broadening</i></p> <p>Andreas Leineweber, Max Planck Institute Stuttgart, D</p>	<p>Plenary Lecture: Lakeside Theaters, Chair: Thomas Hansen</p> <p><i>Microstrain broadening</i></p> <p>Andreas Leineweber, Max Planck Institute Stuttgart, D</p>	8h30
Chemistry AUD I, 1514-213		iNANO building, 1593-012	
9h30	Coffee	Coffee	9h30
	<p>MS07: Diffraction line profile analysis, stress, strain and texture</p> <p>Chairs: Paolo Scardi, University of Trento (IT) Daniel Loüer, Université de Rennes (FR)</p>	<p>MS03: Biological and Molecular Materials</p> <p>Chairs: Andy Fitch, ESRF (Grenoble, F) Kenny Ståhl, Technical University of Denmark (DK)</p>	
10h00	In memory of J.I. (Ian) Langford		10h00
10h10	<p><i>Strain distributions and diffraction peak profiles from crystals with dislocations</i></p> <p>Vladimir Kaganer, Paul-Drude-Institut für Festkörperelektronik (Berlin, DE)</p>	<p><i>Powder Diffraction: Perspectives in Drug Discovery</i></p> <p>F. Karavassili, University of Patras (GR)</p>	10h10
10h40	<p><i>How far can powder diffraction quantify stacking disorder interaction ranges through full pattern analysis?</i></p> <p>Thomas C. Hansen, Institut Laue-Langevin (Grenoble, FR)</p>	<p><i>Advances in Synchrotron XRPD for Enhanced Characterization of Pharmaceuticals</i></p> <p>P.P. Mazzeo, Excelsus Structural Solutions (Swiss) AG</p>	10h40
11h10	<p><i>Stacking fault energy determination using in situ X-ray diffraction</i></p> <p>David Rafaja, Freiberg University of Technology (DE)</p>	<p><i>Using synergy of experimental and computational techniques to solve monomer-trimer dilemma</i></p> <p>D. Š. Jung, University of Zagreb (HR)</p>	11h10
11h25	<p><i>Diffraction Profile Broadening Owing to Vacancies In LaNi5: Simulations and In-Situ Neutron Diffraction</i></p> <p>Timothy A. Webb, Griffith University (AU)</p>	<p><i>Investigating nanocrystalline drugs embedded in a polymeric matrix by Debye Function Analysis</i></p> <p>C. Giacobbe, Università dell'Insubria (Como, IT)</p>	11h25
11h40	<p><i>Analysis of preferential orientation in zirconium samples deformed by uniaxial tension using neutron and X-ray diffraction</i></p> <p>Monika Kucerakova, Czech Technical University in Prague (CZ)</p>	<p><i>Fit of Organic Crystal Structures to PDF Curves</i></p> <p>Dragica Podgorski, Goethe University, (Frankfurt am Main, DE)</p>	11h40
11h55	<p><i>Design and management of a powder diffraction beamline for Line Profile Analysis: a realistic ray-tracing approach</i></p> <p>Luca Rebuffi, University of Trento (IT)</p>	<p><i>Powder Diffraction and DFT Studies of Synthetic Insect Pheromones</i></p> <p>Andy Fitch, ESRF (Grenoble, FR)</p>	11h55
12h10	Lunch (Tent at Chemistry) PANalytical workshop	Lunch (Tent at Chemistry) Lachlan's Software Fayre	12h10

	Monday 16 June 2014 Afternoon	Monday 16 June 2014 Afternoon	
	Chemistry AUD I, 1514-213	iNANO building, 1593-012	
	MS04: Combined Methods for Structure Analysis: Electron diffraction, Powder diffraction & Tomography Chairs: Lynne McCusker, ETH Zurich (CH) Carsten Gundlach, Technical University of Denmark (DK)	MS06: Progress in instrumentation Chairs: Ron Smith, Rutherford Appleton Laboratory (UK) Bob Cernik, SRS, Daresbury (UK)	
13h40	Combining X-ray powder diffraction and 3D imaging Christopher Egan, University of Manchester (UK)	Integrating PXRD in Accelerated Materials Discovery Sam Chong, University of Liverpool (UK)	13h40
14h10	A comparative study of Pd₂Ga/SiO₂: in situ X-ray Diffraction and Electron Microscopy E.M. Fiordaliso, Technical University of Denmark (DK)	In-Situ Neutron Diffraction Studies of Electrode Materials for Li-ion Batteries Matteo Bianchini, ILL (Grenoble, FR)	14h10
14h40	Reveal the crystal structure of nano-size microporous materials by combining RED and PXRD Hong Chen, Stockholm University (SE)	Resolving an instrumental conundrum: Bragg-Brentano and linear detectors Bernd Hinrichsen, BASF SE, (DE)	14h40
14h55	Compact Bone Studied by Diffraction Tomography Mie Birkbak, Aarhus University (DK)	New Facility for Long Duration Experiments at Diamond Claire A. Murray, Diamond Light Source (UK)	14h55
15h10	Study of high temperature transformation of titanate nanotubes Tereza Brunátová, Charles University (Prague, CZ)	Towards routine data collection from hydrogenous materials using powder neutron diffraction Paul F. Henry, European Spallation Source (Lund, SE)	15h10
15h25	Structure analysis from powder having a strong anisotropic shape using a Gandolfi camera A. Ohbuchi, Rigaku Corporation (Tokyo, JP)	HEIMDAL: A time-of-flight neutron powder diffractometer at ESS for in-situ/in-operandi materials science studies Mogens Christensen (Aarhus, DK)	15h25
15h40	Poster & Coffee	Poster & Coffee	15h40
17h30	Plenary lecture: Lakeside Theaters, Chair: Andy Fitch, ESRF From studying the structure and microstructure of crystals formed in nature, to forming new bio-inspired materials Boaz Pokroy, Technion, Israel Institute of Technology, IL	Plenary lecture: Lakeside Theaters, Chair: Andy Fitch, ESRF From studying the structure and microstructure of crystals formed in nature, to forming new bio-inspired materials Boaz Pokroy, Technion, Israel Institute of Technology, IL	17h30
18h30			
19h15	Cultural event AROS, see Program booklet	Cultural event AROS, see Program booklet	19h15

Tuesday 17 June 2014 Morning		Tuesday 17 June 2014 Morning	
8h30	<p>Plenary Lecture: Lakeside Theaters, Chair: Radovan Černý, <u>Accurate and Reliable Molecular Crystal Structures from XRPD and DFT-D: State-of-the-art and Future Directions</u> Jacco van der Streek, University of Copenhagen, DK</p>	<p>Plenary Lecture: Lakeside Theaters, Chair: Radovan Černý, <u>Accurate and Reliable Molecular Crystal Structures from XRPD and DFT-D: State-of-the-art and Future Directions</u> Jacco van der Streek, University of Copenhagen, DK</p>	8h30
Chemistry AUD I, 1514-213		iNANO building, 1593-012	
9h30	Coffee	Coffee	9h30
	<p>MS01: Total Scattering Techniques and Disorder Chairs: Reinhard Neder, University of Erlangen (D) Peter Chupas, Argonne National Laboratory (USA)</p>	<p>MS08: In situ, in operando studies Chairs: Wojciech Paszkowicz, Institute of Physics (Warsaw, PL) Claudia Weidenthaler, Max-Planck-Institut für Kohlenforschung (DE)</p>	
10h00	<p><u>Tracking the formation of zirconia nanoparticles in solution on atomic scale</u> Ann-Christin Dippel, DESY (Hamburg, D)</p>	<p><u>Time and space resolved XRD studies of catalytic reactors</u> David S. Wragg</p>	10h00
10h30	<p><u>Total scattering to access structural information in complex aluminosilicate glasses: the example Zn addition</u> Andrea Bernasconi, ESRF (Grenoble, F)</p>	<p><u>Combining in-situ X-ray techniques and related methods to obtain more information on dynamic systems</u> Hermann Emerich (Grenoble, F)</p>	10h30
11h00	<p><u>Intergrowth quantification by PDF analysis</u> Philippe Deniard, Université de Nantes (F)</p>	<p><u>Formation of γ-Fe₂O₃ in hydrothermal synthesis: In situ total scattering studies</u> Kirsten M. Ø. Jensen, Columbia University (New York, USA)</p>	11h00
11h15	<p><u>Frustration and disorder in simple molecular frameworks</u> Matthew J. Cliffe, University of Oxford (UK)</p>	<p><u>Strain characterisation in Nano-crystalline ceramics: The Laser pump-probe technique</u> Morgan E. Jones, Aberystwyth University (Wales, UK)</p>	11h15
11h30	<p><u>Magic-Sized Clusters and Disordered Shells during Nucleation of ZnO Nanoparticles in Sol-Gel Synthesis</u> Mirijam Zobel, University of Erlangen (D)</p>	<p><u>In-situ Synchrotron and Neutron Diffraction on Phase Transformations in Austempered Ductile Iron (ADI)</u> Xiaohu Li, University of Munich (DE)</p>	11h30
11h45	<p><u>Total scattering investigation of local structure around iron in FeV-based bcc-hydrides</u> Henrik Mauroy, Institute for Energy Technology (Kjeller, N)</p>	<p><u>Reaction pathways and intermediates in the hydrogenation of Zintl phases by in situ neutron powder diffraction</u> Holger Kohlmann, University of Leipzig (DE)</p>	11h45
12h00	<p>Lunch (Tent at Chemistry) Bruker workshop EPDIC committee closed meeting 1510-410</p>	<p>Lunch (Tent at Chemistry) Lachlan's Software Fayre</p>	12h00

	Tuesday 17 June 2014 Afternoon	Tuesday 17 June 2014 Afternoon	
	Chemistry AUD I, 1514-213	iNANO building, 1593-012	
	<p>MS02: Ab initio Structure Solutions</p> <p>Chairs: Anton Meden, University of Ljubljana (SI) Vincent Favre-Nicolin, CEA (Grenoble, F)</p>	<p>MS11: Structure and properties of functional materials</p> <p>Chairs: Matt Tucker, ISIS Facility (UK) Helmut Ehrenberg, KIT, IAM-ES (Karlsruhe, DE)</p>	
13h30	<p>Structure solution of molecular compounds using direct-space local LS minimizations and cluster-based direct methods</p> <p>Oriol Vallcorba, ALBA-CELLS, Synchrotron Light Source (Barcelona, ES)</p>	<p>Neutron Diffraction Studies of Fuel Cell Materials</p> <p>Stephen Hull, ISIS Facility (UK)</p>	13h30
14h00	<p>Difficult structures come in a variety of flavors</p> <p>Stef Smeets, ETH Zurich (CH)</p>	<p>Local Off-Centering Symmetry Breaking in the High-Temperature Regime of SnTe</p> <p>Emil Bozina, Brookhaven National Laboratory (New York, USA)</p>	14h00
14h30	<p>Structural characterization of highly defective metal nitropyrazolates by a combination of Rietveld and Debye Function Analyses</p> <p>Federica Bertolotti, Universita dell'Insubria (I)</p>	<p>Structure, electric and magnetic properties of $Pb(V_{1-x}M_x)O_3$, $M=Ti, Fe$ compounds</p> <p>Pierre Bordet, Universite Grenoble Alpes (FR)</p>	14h30
14h45	<p>SDPD of nanocrystalline organic compounds without prior indexing using a fit by similarity measure based on cross-correlation functions</p> <p>Martin U. Schmidt, Goethe University, Frankfurt am Main (D)</p>	<p>Study of Charge-ordering in $Pr_{0.5}Ca_{0.5}MnO_3$ via Serial Femtosecond Crystallography</p> <p>Kenneth R. Beyerlein, Center for Free-Electron Laser Science (DE)</p>	14h45
15h00	<p>The crystal structure of the new $Rb_2MnP_2O_7 \cdot H_2O$ diphosphate - ab initio determination from X-ray powder diffraction data</p> <p>Stanislav Péchev, Université de Bordeaux (FR)</p>	<p>Location of CO_2 guest molecules during its uptake by the flexible porous MOF MIL-53(Fe)</p> <p>Guillou Nathalie, University of Versailles (FR)</p>	15h00
15h15	<p>Accurate bond lengths from XRPD via meta-refinement</p> <p>Ivan S. Bushmarinov, Institute of Organoelement Compounds RAS (Moscow, RU)</p>	<p>Mapping topology and structural disorder in $[M(CN)_2]^-$ coordination polymers</p> <p>Joshua A Hill, University of Oxford (UK)</p>	15h15
15h30	<p>Poster & Coffee</p>	<p>Poster & Coffee</p>	15h30
17h30	<p>Plenary lecture: Lakeside Theaters, Chair: Poul Norby</p> <p>X-Rays and neutrons as essential tools for lithium battery research</p> <p>Christian Masquelier, Universite de Picardie Jules Verne Amiens, F</p>	<p>Plenary lecture: Lakeside Theaters, Chair: Poul Norby</p> <p>X-Rays and neutrons as essential tools for lithium battery research</p> <p>Christian Masquelier, Universite de Picardie Jules Verne Amiens, F</p>	17h30
18h30			18h30
19h00	<p>Conference Dinner</p> <p>Stakladen, see Program booklet</p>	<p>Conference Dinner</p> <p>Stakladen, see Program booklet</p>	19h00

Wednesday 18 June 2014 Morning		Wednesday 18 June 2014 Morning	
8h30	<p>Plenary Lecture: Lakeside Theaters, Chair: Thomas Hansen <i>Neutron Diffraction: Current Achievements at a Long Pulse Neutron Source</i> Denis Kozlenko, Institute for Nuclear Joint Research, Dubna, RUS</p>	<p>Plenary Lecture: Lakeside Theaters, Chair: Thomas Hansen <i>Neutron Diffraction: Current Achievements at a Long Pulse Neutron Source</i> Denis Kozlenko, Institute for Nuclear Joint Research, Dubna, RUS</p>	8h30
Chemistry AUD I, 1514-213		iNANO building, 1593-012	
9h30	Coffee	Coffee	9h30
	<p>MS09: Nanomaterials, surfaces and interfaces Chairs: Matteo Leoni, University of Trento (IT) Nina Lock, Aarhus University (DK)</p>	<p>MS10: Neutron Structural and Magnetic Scattering Chairs: Denis Kozlenko, Joint Institute for Nuclear Research (Dubna, RU) Oksana Zaharko, Paul Scherrer Institut (CH)</p>	
10h00	<p><i>High-energy surface X-ray diffraction applied to model catalysis</i> Johan Gustafson, University of Lund (SE)</p>	<p><i>Correlated Disorder in Functional Materials</i> Andrew L. Goodwin, University of Oxford (UK)</p>	10h00
10h30	<p><i>X-ray imaging of single nano-crystals</i> Vincent Favre-Nicolin, CEA-UJF (FR)</p>	<p><i>Towards sodium ion batteries: understanding sodium dynamics on a microscopic level</i> Marisa Medarde, Paul Scherrer Institut (CH)</p>	10h30
11h00	<p><i>Nanocrystalline powder diffraction as a surface science tool</i> Zbigniew Kaszukur, Polish Academy of Sciences (PL)</p>	<p><i>Interplay between spin and lattice degrees of freedom in VF_3</i> Gwilherm Nénert, PANalytical (Almelo, NL)</p>	11h00
11h15	<p><i>Novel method for solving and refining the structure of thin film phases using Cu x-ray radiation and 2D detectors.</i> Carlos Frontera, Institut de Ciencia de Materials de Barcelona (ES)</p>	<p><i>Nature of Partial Magnetic Order in $Gd_2Ti_2O_7$</i> Joseph Paddison, University of Oxford (UK)</p>	11h15
11h30	<p><i>Modelling the diffraction pattern of faulted nanocrystals</i> Robert Koch, University of Trento (IT)</p>	<p><i>Powder Diffraction Study of Structural and Magnetic Transitions in Oxygen Deficient Complex Cobalt Oxides</i> Vadim Sikolenki, Helmholtz Center Berlin (DE)</p>	11h30
11h45	<p><i>Unravelling the growth of Pt nanorods inside a porous matrix by Debye Function Analysis</i> Antonietta Guagliardi, Istituto di Cristallografia (Como, IT)</p>	<p><i>Electric polarization from spiral order below 200K in multiferroic $YBaCuFeO_5$</i> Mickaël Christian. Morin, Paul Scherrer Institut (CH)</p>	11h45
12h00	Lunch (Tent at Chemistry) Rigaku workshop	Lunch (Tent at Chemistry) Lachlan's Software Fayre	12h00

	Wednesday 18 June 2014 Afternoon	Wednesday 18 June 2014 Afternoon	
	Chemistry AUD I, 1514-213	iNANO building, 1593-012	
	MS05: Energy Materials Chairs: Bill David, ISIS Facility (UK) Dorthe Bomholt Ravnsbæk, Aarhus University (DK)	MS12: Diffraction under pressure Chairs: Martin Bremholm, Aarhus University (DK) Leonid Dubrovinsky, University of Bayreuth (DE)	
13h30	Powder Diffraction Studies of Metal Hydrides Proposed for Concentrated Solar Thermal Energy Storage Applications Craig Buckley, Curtin University (AU)	Advanced synchrotron techniques to study materials in-situ at high pressure and temperature Vitali B. Prakapenka, University of Chicago (USA)	13h30
14h00	Watching nanocrystals form Bo B. Iversen, Aarhus University (DK)	Neutron Diffraction at High Pressure at IBR-2 Reactor: Current State and Prospects Sergey Kichanov, Joint Institute for Nuclear Research (RUS)	14h00
14h30	Decomposition Pathways of Complex Hydrides with Metal Sulphides Mark Paskevicius, Curtin University, (AU)	Critical behaviour in molecular frameworks: understanding the origin of negative thermal expansion in zinc (II) cyanide Andrew B. Cairns, University of Oxford (UK)	14h30
14h45	Thermodynamics and Crystal Structures of the Alkali Silanides MSiH₃ (M=K, Rb, Cs) Jean-Noel Chotard, Université de Picardie Jules Verne (FR)	Dramatic softening of the negative thermal expansion material HfW₂O₈ on heating through its WO₄ orientational order-disorder phase transition Leighanne Gallington, Georgia Institute of Technology (USA)	14h45
15h00	Borohydrides: in situ powder diffraction and Li-rich topologies Radovan Černý, University Geneva (CH)	K₂CO₃ at high pressures: powder diffraction experiment and structure prediction Pavel Gavryushkin, Russian Academy of Sciences, Siberian Branch (RU)	15h00
15h15	Transition Metal Based Catalysts for Ammonia Decomposition Claudia Weidenthaler, Max-Planck-Institut für Kohlenforschung (DE)	Microstructure defects in graphitic boron nitride: Analysis, modification and impact on the transition to sp³-hybridized BN Christian Schimpf, TU Bergakademie Freiberg (DE)	15h15
15h30	Coffee	Coffee	15h30
16h00	Plenary lecture: Lakeside Theaters, Chair: Michela Brunelli Non-stoichiometry in correlated oxide materials studied by in situ diffraction methods Monica Ceretti, Institut Charles Gerhardt, Montpellier, F	Plenary lecture: Lakeside Theaters, Chair: Michela Brunelli Non-stoichiometry in correlated oxide materials studied by in situ diffraction methods Monica Ceretti, Institut Charles Gerhardt, Montpellier, F	16h00
17h00	Closing Ceremony – Lakeside Theaters Chair: Jens-Erik Jørgensen Honorary Lecture: <i>Strain mechanisms in actuators: in operando investigation of functional materials</i>	Closing Ceremony – Lakeside Theaters Chair: Jens-Erik Jørgensen Honorary Lecture: <i>Strain mechanisms in actuators: in operando investigation of functional materials</i>	17h00
18h00	Manuel Hinterstein, University of New South Wales, AU	Manuel Hinterstein, University of New South Wales, AU	18h00

Opening Lecture:

“Crystallography - past, present and future”

Prof. Sine Larsen, University of Copenhagen, Denmark

Crystallography and powder diffraction past, present and future

[Sine Larsen](#)

Department of Chemistry, University of Copenhagen, Denmark. e-mail: sine@chem.ku.dk

The centennial of the birth of modern crystallography is an important part of the celebration of the International Year of Crystallography during 2014. It is natural to look back and forward on the development of our science. In the historical perspective it is interesting to note that the theoretical foundation of crystallographic science was developed within a very short period (around 20 year) after Max von Laue's seminal experiment with X-rays in 1912. Though the theory was in place it was not before the advent of computers in the mid 1960es that X-ray crystallography became the most powerful tool for accurate structure determination at atomic resolution of crystalline materials. The computers were driving the development of experimental equipment and software that enabled structure determination by "direct methods", leading to an exponential growth of the crystal structures of inorganic and organic compounds. The success of crystallography and its impact on other sciences that depend on structural information were so great that it almost threatened its role as an independent scientific area. Recording the diffraction from powdered samples by photographic films represent techniques that first was used with great success in industry and academia and have benefitted from the development of advanced software.

The availability of new neutron and X-ray sources (synchrotrons) opened new exciting avenues for powder diffraction, the ability to study very small (micron-sized) crystals and to combine different X-ray/neutron based techniques.

The International Union of Crystallography (IUCr) has as a learned society publisher for the last 65 years been a leading in publishing crystallographic results, but it has also had an important role in maintaining and developing the identity of the crystallographic community. The crystallographic conferences and meetings show the richness and diversity of crystallography as a science in itself and how it underpins related sciences.

Keywords: crystallography, centennial, large X-ray and neutron facilities

Honorary Lectures:

Lakeside Theaters

“Laboratory X-ray powder diffraction at the University of Rennes: an overview”

Prof. Daniel Louër, University of Renne, France

“Strain mechanisms in actuators: in operando investigation of functional materials”

Dr. Manuel Hinterstein, University of New South Wales, Australia

Opening Honorary Lecture

Laboratory X-ray powder diffraction at the University of Rennes: an overview

[Daniel Louër](#)

Chantepie, Brittany, France (formerly University of Rennes I, France) e-mail: daniel.louer@free.fr

Advances in methodology, instrument resolution and computer technology have contributed to the development of modern powder diffraction. The technique with monochromatic laboratory X-rays has been used at the University of Rennes since 1964, for applications in solid state chemistry and reactivity of solids. A particular attention has been paid to the accuracy of measurements with diffractometers based on Bragg-Brentano geometry. The instrument resolution function and line profile shapes were precisely modeled with profile fitting techniques in the 1980s and position-sensitive detectors were used for temperature-dependent diffraction studies. The methodology and software have been continuously adapted and improved according to the significant changes occurred in powder diffraction and computer technology. A first important application has been the interpretation of diffraction line broadening for nanopowders obtained in chemical reactions. The microstructural properties were first determined from the analysis of well resolved lines in the pattern by means of local computer programs for deconvolution, Fourier and integral breadth analyses. With the advent of profile fitting and pattern decomposition techniques in the 1980s, more diffraction lines were available, and a wealth of information could be obtained from line profile analysis. This is illustrated with representative studies on nanocrystalline powders characterized in terms of crystallite size, shape, microstrain or stacking fault probability. The second major application has been structure determination from powder data. With the progress made in instrument resolution, pattern indexing with the dichotomy method, pattern decomposition software, the Rietveld method applied to X-ray diffraction data and experience with single-crystal diffraction methods, the Rennes group has been interested in *ab initio* structure determination from powder data in the 1980s. Some examples have been selected to point out the importance of this application in chemistry.

Keywords: Instrument resolution, microstructure, indexing method, structure determination, monochromatic X-rays, non-ambient powder diffraction

Closing Honorary Lecture

Strain mechanisms in actuators: in operando investigation of functional materials

[Manuel Hinterstein](#)

University of New South Wales, AU

The function of materials widely depends on the crystalline structure and the modification of that structure during the application. In the special case of piezoelectric actuators an applied electric field couples elastic strain and polarization. Among the various types of piezoelectric devices only actuators rely on high electric fields to generate high strains and forces. Prominent examples for actuators are multilayer stack actuators used for nanopositioning or in modern combustion engines for automobiles to control injection cycles. Despite extensive studies and elaborated measurement techniques, the correlation between macroscopic strain and structural response is still not fully understood.

Most of the relevant systems found up to now are compositions close to phase boundaries linking highly correlated phases. This results in major challenges for structural analyses due to overlapping reflections. Apart from the well-known field induced structural responses such as domain switching and the piezoelectric effect we recently identified field induced phase transitions in different systems as an additional poling mechanism [1,2]. The development of a structural analysis of in operando powder diffraction data allows resolving all three involved poling mechanisms within only one experiment. The key to obtain enough information for such an analysis is a combination of high resolution and a broad Q-range, together with different sample orientations. This can be done with either X-ray or Neutron powder diffraction. The results not only separately reveal the contributions of each poling mechanism to the macroscopic strain, but also different behaviours of the individual phases.

[1] M. Hinterstein, M. Knapp, M. Hoelzel, W. Jo, A. Cervellino, H. Ehrenberg and H. Fuess, *J. Appl. Phys.* **43**, 1314 (2010).

[2] M. Hinterstein, J. Rouquette, J. Haines, Ph. Papet, M. Knapp, J. Glaum and H. Fuess, *Phys. Rev. Lett.* **107**, 077602 (2011).

Plenary Lectures

Lakeside Theaters

Microstrain broadening

[Andreas Leineweber^a](#)

^aMax Planck Institute for Intelligent systems (formerly Max Planck Institute for Metals Research), Stuttgart, Germany

Microstrain broadening is, in many cases, immediately associated with the distortion fields caused by the presence of dislocations. This is definitely caused by the considerable interest in plastically deformed matter but also in the fair success of various approaches to relate observed microstrain broadening with dislocations densities and their line- and Burgers vectors.

It can, however, be shown that the realm of origins of microstrain broadening is much more extended. It should be recognised that strain, i.e. a relative length change, should be associated in the context of diffraction with a relative change in d spacing. Thereby, the strain is not necessarily caused by stresses but it can also originate from composition or temperature change. Presence of microstrain then implies that the origins of strain, e.g. composition, temperature or stress, are distributed over the specimen under consideration. In many cases the local strain gradients are sufficiently small. In that case the probability-density function of strain (along the diffraction vector) is directly visible as a line-broadening contribution in a powder-diffraction pattern [1,2]. Prediction of the observed profiles is, however, considerably complicated if the strain gradients are sufficiently short-ranged so that interference occurs between differently strained regions [2].

Various model cases of microstrain broadening will be discussed focusing, in particular, on anisotropy of the microstrain broadening facilitating identification of the origin of the underlying microstrain. That identification is, in turn, basis for quantification of the variations in e.g. composition, temperature and stress on the basis of the observed broadening. Moreover, the diffraction effects exhibited by different microstructures containing short-ranged strain gradients and other related short-range inhomogeneities [2,3] will be discussed.

[1] A. Leineweber, *Z. Kristallogr.* 2011, 226, 905 [2] A. Leineweber, E.J. Mittemeijer, *J. Appl. Cryst.* 2010, 43, 981 [3] A. Leineweber, F. Krumeich, *Phil. Mag.* 2013, 93, 4440.

Keywords: line-broadening analysis, microstrain

From studying the structure and microstructure of crystals formed in nature, to forming new bio-inspired materials

[Boaz Pokroy^a](#)

^aMaterials Science and Engineering and the Russell Berrie Nanotechnology Institute, Technion, Israel, e-mail: bpokroy@tx.technion.ac.il

Nature is replete with materials which are superior to their man-made counterparts. More specifically, in the course of Biomineralization (the formation of minerals in nature) at least 70 biominerals are deposited. The nucleation and growth of these crystals is highly controlled via specific organic/inorganic interfaces.

These hybrid interfaces are present both between crystallites (intercrystalline) as well as within crystals themselves (intracrystalline). The latter have been found to induce distortion in the inorganic crystalline host. This incorporation leads not only to deformation of the lattice but also to unique microstructural characteristics as compared to their non-biogenic counterparts.

Utilizing high-resolution synchrotron powder diffraction we were able to measure these anisotropic distortions and changes in microstructure. We show that upon mild annealing we can destroy these hybrid interfaces, leading to the relaxation of the lattice strains and to the crystal structure returning to a structure identical to its non-biogenic counterparts [1].

It will also be shown that biomimetic crystals, which are grown in the lab, can beautifully mimic these structural and microstructural aspects and shed additional light on some of the biological mechanisms [2]. We further show that we can use this phenomenon of intracrystalline incorporation and lattice distortions to engineer the band gap of different semiconductors in a controlled manner [3].

[1] Pokroy B, Fitch AN, Zolotoyabko E. *Adv. Mater.* 2006;18: 2363. [2] Borukhin S, Bloch L, Radlauer T, Hill AH, Fitch AN, Pokroy B. *Adv. Funct. Mater.* 2012;22: 4216. [3] Brif A, Ankonina G, Drathen C, Pokroy B. *Adv. Mater.* 2014;26: 477.

Keywords: Biomineralization, High Resolution Powder Diffraction, Bio-Inspired Crystal Growth, Band Gap Engineering.

Accurate and Reliable Molecular Crystal Structures from XRPD and DFT-D: State-of-the-art and Future Directions

Jacco van de Streek^a

^aUniversity of Copenhagen, Denmark, e-mail: jacco.vandestreek@sund.ku.dk

Dispersion-corrected Density Functional Theory (DFT-D) has been shown to reproduce molecular crystal structures very accurately. In a validation study, the average Root Mean Square (RMS) Cartesian displacement upon energy-minimisation with the unit cell free was only 0.084 Å [1]. Incorrect crystal structures could be distinguished based on their significantly higher RMS values. This makes DFT-D highly suitable as a source of complementary data for confirming the correctness of a crystal structure determined from powder diffraction data.

However, there is another use for DFT-D calculations in crystal structure determination from powder data. Experimental X-ray powder diffraction data, especially laboratory data, is often limited to a real-space resolution of about 1.5 Å: enough to locate a molecule as a whole very accurately, but not enough to refine bond lengths and bond angles with great accuracy. Molecular geometries from DFT-D reproduce high-quality single crystal geometries with an accuracy of about 0.02 Å on bond lengths. The DFT-D calculations can be used as an independent source of information that can be fed into the Rietveld refinement in the form of polymorph-dependent restraints, for example in the program *TOPAS* [2].

The combination of XRPD and DFT-D is therefore able to produce molecular crystal structures that are both more reliable and more accurate than would be possible through the use of XRPD alone [3].

Recently, we have started to use Molecular Dynamics (MD) simulations to include the effect of thermal motion, *e.g.* to describe the disorder in simvastatin in detail. In the future, combining the DFT-D calculations with MD simulations will allow us to solve disordered molecular crystal structures from laboratory X-ray powder diffraction data with great accuracy and reliability.

[1] J. van de Streek & M. A. Neumann, *Acta Cryst.* 2010, B66, 544
 [2] A. A. Coelho (2012), *TOPAS-Academic* version 5, Coelho Software. [3] K. Naelapää, J. van de Streek, J. Rantanen & A. D. Bond, *J. Pharm. Sci.* 2012, 101, 4214.

Keywords: molecular crystal structure, Rietveld refinement, DFT

X-Rays and neutrons as essential tools for lithium battery research

Christian Masquelier^a, Laurence Croguennec^b, Mathieu Morcrette^a, Robert Dominko^c, Gwenaëlle Rousse^d, Jean-Noël Chotard^a, Jean-Bernard Leriche^a

^aLRCS, UPJV Amiens, France

^bICMCB Bordeaux, CNRS, France

^cNIC Ljubljana, Slovenia

^dUPMC, Paris, France

Polyanion-based positive electrodes have been widely investigated for more than a decade since the rising success of the LiFePO₄ composition, a major player nowadays for power tool, stationary storage and hybrid electric vehicles applications. Phosphates (LiMPO₄, Li₃M₂(PO₄)₃, FePO₄.nH₂O, MOPO₄, ..), fluorophosphates (LiMPO₄F), fluoro-sulphates (Li₂MSO₄F), silicates (Li₂MSiO₄), di-phosphates (Li₂MP₂O₇), borates (LiMBO₃) have been proposed (M = Fe, Mn, V, Ti). They offer extremely rich crystal chemistry, both at the synthesis level and during electrochemical operation [1]. Among them, our efforts recently focused on highly defective Li_xFe_yPO₄ compositions [2-3], on the rich polymorphism of Li₂FeSiO₄ [4-6] and on the 2 electrons fluorophosphate LiVPO₄F [7].

We will focus in this presentation on latest results on the precise crystal chemistry (synthesis procedures, crystal structures, mechanisms of Li⁺ extraction/insertion) of compositions of special interest, through extensive use of synchrotron X-Ray and neutron diffraction, in particular *in situ* during battery operation.

[1] C. Masquelier, L. Croguennec, *Chemical Reviews*, 113(8), 6552-6591 (2013)
 [2] S. Hamelet et al, *J. Mater. Chem.*, 19, 3979 (2009) ; *Chem. Mater.*, 23, 32-38 (2011)
 [3] R. Amisse et al., *J. Electrochem. Soc.*, **160**(9), A1446-A1450 (2013)
 [4] A. Boulineau et al., *Dalton Transactions*, 39, 6310 (2010)
 [5] C. Sirisopanaporn et al., *Inorg. Chem.*, 47, 7446 (2010) ; *J. Am. Chem. Soc.*, **133**, 1263-1265 (2011)
 [6] S. Islam et al., *J. Mater. Chem.*, **21**, 9811-9818 (2011)
 [7] J.M. Ateba Mba et al., *Chem. Mater.*, **24**(6), 1223 (2012) ; *J. Electrochem. Soc.*, **159**(8), A1171 (2012)

Keywords: Phosphates, Li-Ion batteries

Neutron Diffraction: Current Achievements at a Long Pulse Neutron Source

[D.P. Kozlenko](#)

*Frank Laboratory of Neutron Physics, Joint Institute for Nuclear Research,
141980 Dubna, Russia*

The powder neutron diffraction is a classical neutron scattering technique, which development has been started soon after discovery of neutron by J. Chadwick. Following the evolution of the neutron sources, now it becomes one of the most frequently used neutron scattering methods for the analysis of crystal and magnetic structure of materials and relationship of its features with physical properties, providing important information for priority topics of condensed matter physics, materials science, chemistry, geosciences, biophysics, etc.

The general introduction to neutron diffraction is given and its specific features in comparison with X-ray diffraction are considered. Taking into account a current interest of the scientific community in development of the long pulse neutron sources (like ESS project), the realization of neutron diffraction techniques at the IBR-2 high flux pulsed reactor, having the longest duration of the neutron pulse among acting neutron sources is presented. The standard and specific experimental techniques, like reverse time-of-flight methods, are considered.

The recent research topics, including structural studies of hydrogen storage materials, charging/discharging processes of Li-accumulators, materials under extreme conditions, magnetic oxide and intermetallic compounds, residual stresses in materials, texture of rocks and minerals, are overviewed.

Non-stoichiometry in correlated oxide materials studied by *in situ* diffraction methods

[Monica Ceretti^a](#)

*^aInstitut Charles Gerhardt, UMR 5253, Université de Montpellier 2, Place Eugène Bataillon, 34095 Montpellier, France
monica.ceretti@univ-montp2.fr*

Complex ordering phenomena and associated changes in the physical and chemical properties are common features of correlated non-stoichiometric oxides. Changes of the oxygen stoichiometry can proceed at already ambient temperature controlled by electrochemical methods, allowing to establish metastable phases showing long range oxygen ordering, generally not available at high temperature. Typical examples are some Brownmillerite and Ruddlesden-Popper type oxides, which are able to take up reversibly oxygen ions. We show here that *in-situ* diffraction techniques (neutron and synchrotron), combined with X-rays absorption spectroscopy, are very powerful to explore their structural and electronic phase diagrams [1, 2]. By controlling oxygen content, using specially designed electrochemical cells for *in-situ* diffraction experiments, it was possible to correlate structural evolution with the charge transfer and to identify reaction intermediates showing complex oxygen ordering. Particular attention will be paid on K_2NiF_4 type structure, as R_2MO_{4+d} ($R = La, Nd, Pr, \dots, M = Cu, Ni, Co, \dots$), where structural correlations, going far beyond the limits reported for homologous phases using cation substitution, have been observed [3]. From *in-situ* diffraction data, structural complexity has been explored by the Maximum Entropy Method, involving an anharmonic displacement of the diffusing oxygen species, underlying the importance of lattice dynamics contribution for oxygen diffusion at low temperature [4, 5].

[1] R. Le Toquin et al, Journal of the American Chemical Society, (2006) 128, 13161-13174. [2] A. Piovano et al, The Journal of Physical Chemistry C, (2010) 115 1311-1322. [3] L. Le Dréau et al, Inorganic Chemistry, (2012) 51 9789-9798. [4] A. Villesuzanne et al, Journal of Solid State Electrochemistry, (2011) 15 357-366. [5] W. Paulus et al, Journal of the American Chemical Society, (2008) 130 16080-16085.

Keywords: *in-situ* studies, powder neutron diffraction, x-rays diffraction, non-stoichiometric oxides

*Microsymposium MS01:
Total Scattering Techniques and Disorder*

Chairs: Reinhard Neder, University of Erlangen (D)

Peter Chupas, Argonne National Laboratory (USA)

Microsymposium: Tuesday 17 June 2014 Morning – Chemistry AUD I, 1514-213

Poster session: Tuesday 17 June 2014 – iNANO building, 1590-Foyer

Keynote Lecturers:

MS01_K1

Tracking the formation of zirconia nanoparticles in solution on atomic scale

[Ann-Christin Dippel](#)^{a,b}, [Christoffer Tyrsted](#)^b, [Kirsten M. Ø. Jensen](#)^{b,c}, [Dipankar Saha](#)^b, [Steinar Birgisson](#)^b & [Bo B. Iversen](#)^b

^aDeutsches Elektronen-Synchrotron DESY, Hamburg, Germany

^bCenter for Materials Crystallography, Department of Chemistry and iNANO, Aarhus University, Denmark

^cApplied Physics and Applied Mathematics, Columbia University, New York, USA

e-mail: ann-christin.dippel@desy.de

Wet-chemical synthesis is a common bottom-up approach to fabricate nanoparticles in different compositions, sizes, and shapes. Frequently used techniques include redox-based reactions, (microemulsion-mediated) sol-gel processes, solvothermal synthesis, and ultrasound and/or microwave assisted routes. In general, the morphology and structural characteristics of the nanoparticles inherently determine their macroscopic properties such as catalytic activity, conductivity, colour, and selective physisorption. Therefore, it is essential to control the underlying microscopic features, e.g. diameter, aspect ratio, and crystal structure, in order to effectively tailor the nanoparticles for specific applications. Yet, the knowledge about how to steer a reactions in a particular direction is mostly empirical. A detailed understanding of the reaction pathway is best obtained by following the transitions by *in situ* probing techniques in real time. In the case of nanoparticles, time-resolved high-energy x-ray powder diffraction is an ideal tool for this purpose as it provides access to the pair distribution function (PDF) and, thus, the short and medium range order of the material under investigation. This holds true also for the mostly amorphous or cluster-like dissolved precursors and intermediates.

Recently, the power of *in situ* PDF analysis to reveal the reaction mechanism during nanoparticle formation was demonstrated [1]. In a similar methodology, the structural changes during the formation of yttria stabilized zirconia under supercritical conditions were described on atomic scale for the entire course of reaction [2]. The study presented here shows the results from the time-resolved PDF analysis of pure zirconia nanoparticles prepared by hydrothermal synthesis. As in the yttria stabilised case, the polymeric reactant undergoes amorphisation before crystallisation is induced. However, the respective choice of reaction conditions (e.g. starting materials and temperature) leads to crucial differences in kinetics, phase selection,

and crystallite growth in both synthesis routes and, hence, gives certain control over the crystal structure and size of zirconia nanoparticles.

[1] K. M. Ø. Jensen, M. Christensen, P. Juhas, C. Tyrsted, E. D. Bøjesen, N. Lock, S. J. L. Billinge, B. B. Iversen, *J. Am. Chem. Soc.* 2012, 134, 6785. [2] C. Tyrsted, N. Lock, K. M. Ø. Jensen, M. Christensen, E. D. Bøjesen, H. Emerich, G. Vaughan, S. J. L. Billinge, B. B. Iversen, to be published.

Keywords: zirconia, nanoparticles, pair distribution function, *in situ* experiments, high-energy x-ray powder diffraction

MS01_K2

Total scattering to access structural information in complex aluminosilicate glasses: the example Zn addition

[Andrea Bernasconi](#)^a, [Monica Dapiaggi](#)^b, [Alessandro Pavese](#)^b & [Daniel T. Bowron](#)^c

^aEuropean Synchrotron Radiation Facility, France

^bUniversity of Milan, Italy

^cISIS Neutron Spallation Sources, UK, e-mail: andrea.bernasconi@esrf.fr

Pair distribution function analysis is one of the most useful techniques adopted to investigate disordered materials, especially in the case of glasses, due to their lack of long range order and periodicity which precludes the use of conventional crystallography. In the present study, Empirical Potential Structure Refinement modeling [1] has been applied to two distinct sets of complex aluminosilica-based glasses with different Zn amounts. Data come from neutron and x-ray total scattering experiments which were performed at the ISIS neutron spallation source and at the European Synchrotron Radiation Facility. With EPSR, structural information like bond angles and distances, and coordination numbers have been obtained; additionally, polymerization degree (bridging oxygen, not-bridging and tricluster) and large cation role (charge compensator or network modifier) have been extracted by a careful overlook of the final configuration provided by the refinement. The first series, which is characterized by a fixed network modifying element content (i.e. Na), shows how the introduction of Zn at the expense of network forming elements (i.e. Si and Al) may replace these latter cations in a tetrahedral arrangement, without altering significantly the polymerization degree. On the other side, the second series, which is characterized by fixed network forming element contents (i.e. Si and Al), shows how the replacement of a network modifying element (i.e. Ca) with the introduction of Zn does not

change the tendency of Zn to be mainly 4-fold coordinated, by promoting the tetrahedral network and, consequently, by influencing some technological properties like the glass transition temperature.

Moreover, a comparison between our results and classical theoretical approaches, like stoichiometric models based on Zachariasen's rules [2] and computational routines [3], have been performed.

[1] A.K. Soper, EPSRshell; A User's Guide, 2010 [2] W.H. Zachariasen, *Journal of American Chemical Society*. 1932, 54 (10), 3841 [3] J.D. Gale, General Utility Lattice Program, Version 4.0, 2011.

Keywords: glass, total scattering

Oral Presentations:

MS01_O1

Intergrowth quantification by PDF analysis.

Philippe Deniard, Kévin Galliez^b, Pierre-Emmanuel Petit^a, David Lambertin^b, Florence Bart^b & Stéphane Jobic^a

^aInstitut des Matériaux Jean Rouxel (IMN) - Université de Nantes, CNRS, 2 rue de la Houssinière, BP 32229, 44322 Nantes cedex 3, FRANCE,

philippe.deniard@cnrs-imn.fr
^bCEA, DEN, DTCD/SPDE/LP2C – Marcoule, 30207 Bagnols-sur-Cèze, FRANCE.

In this presentation, we propose for the very first time an *ab initio* method for quantifying the intergrowth of two structures via a "direct space" pattern refinement using a Pair Distribution Function analysis (PDF). Our procedure consists in modeling the material as a simple mixture of the two sub-structures. Of course, such an approach does not take into account the intergrowth zone in details, i.e. a region where the interatomic distances are subject to relaxation to match the two structure types. However, we show that, in the refinement process, the scale factors of the two sub-structures are not affected by this mismatch of observed and calculated $G(r)$ functions, provided the r calculation range is large enough.

The technique was applied to seven different γ -MnO₂ (R-MnO₂ / β -MnO₂ intergrowth) samples [1]. Results, i.e. the calculated R-MnO₂ / β -MnO₂ ratios in γ -MnO₂, compare perfectly with those issued from the well established quantification technique developed by Chabre and Pannetier [2] which effectiveness is proven. The advantage of our method is clearly that it allows determining the intergrowth rate in a single step refinement and that the standard operating procedure can be easily extrapolated to other kinds of materials without re-determination of lookup tables.

Comparatively to a staking fault approach with a tool such as DIFFax [3], assuming that the aim is just to determine the intergrowth amount, the method developed here does not require to generate numerous and time-consuming models.

We will conclude by a robustness test of the method via the analysis of a γ -MnO₂/Ag₂O blend.

[1] Galliez, K., Deniard, P., Petit, P.-E., Lambertin, D., Bart, F. & Jobic, S. *J. Appl. Cryst.* 2014. 47, doi:10.1107/S1600576714000375

[2] Sarciaux, S., A. Le Gal La Salle, A. Verbaere, Y. Piffard, D. Guyomard. *Journal of Power Sources* 1999. 81–82: 656-660. [3] Treacy, M. M. J., J. M. Newsam, and M. W. Deem. 1991. *Proceedings of the Royal Society of London. Series A: Mathematical and Physical Sciences* 433 499-520.

Keywords: Intergrowth, PDF, quantification, modeling

MS01_O2

Frustration and disorder in simple molecular frameworks

Matthew J. Cliffe^a, Andrew B. Cairns^a, Joseph A. M. Paddison^a & Andrew L. Goodwin^a

^aUniversity of Oxford, UK, e-mail: matthew.cliffe@chem.ox.ac.uk

Frustrated magnets - that is, systems where magnetic interactions compete with each other or with the lattice geometry - have been the subject of intensive investigation in recent years as physicists, chemists and crystallographers have tried to understand both their profoundly disordered magnetic structures and their surprising properties. The collective states and behaviour that emerge from these frustrated interactions are of particular interest, most prominently the discovery that excitations in the spin ice compounds ($\text{Dy}_2\text{Ti}_2\text{O}_7$, $\text{Ho}_2\text{Ti}_2\text{O}_7$) would behave as magnetic monopoles [1][2]. Physical realisations of this physics have thus far been primarily confined to inorganic magnetic materials, where due to the nature of the interactions the most interesting states occur at extremely low temperatures (<50 mK). There is therefore interest in being able to generalise this physics to analogous systems.

One such class of materials are molecular frameworks, which can display correlated structural disorder that closely mimics that of the correlated magnetic disorder in frustrated magnets. For example, the off-centering of Cd^{2+} in $\text{Cd}(\text{CN})_2$ is analogous to the orientation of the magnetic spin in the spin ices[3].

This talk will explore the extent to which structural order and disorder in these simple transition metal salts can be interpreted in terms of a range of canonical models of geometric frustration usually applied in the field of frustrated magnetism.

[1] S. T. Bramwell *et al.*. *Phys. Rev. Lett.* 87, 047205 (2001)

[2] C. Castelnovo *et al.*. *Nature* 451, 42 (2008)

[3] V. E. Fairbank *et al.*. *Phys. Rev. B* 86, 104113 (2012)

Keywords: frustration, disorder, total scattering, molecular frameworks

MS01_O3

Magic-Sized Clusters and Disordered Shells during Nucleation of ZnO Nanoparticles in Sol-Gel Synthesis

M. Zobel^a & R. B. Neder^a

University of Erlangen, Germany, e-mail: mirijam.zobel@fau.de

Semiconductor nanoparticles such as zinc oxide (ZnO) are commonly produced in sol-gel processes. The final nanoparticle powders are well characterized with respect to their crystallinity, which fundamentally governs their physical and chemical properties. Nevertheless, the nucleation process and the evolution of crystallinity of the nucleating nanoparticles is not yet understood [1]. With the advent of the Rapid Acquisition Pair Distribution Function (RA-PDF) method, time-resolved studies have become possible. Smallest molecular clusters of zirconiasulfate oligomers became accessible [2] and the precursor formation and growth of SnO_2 nanoparticles in hydrothermal synthesis could be followed [3]. However, nucleation in dilute sol-gel processes in more complex organic solutions remained obscured [1]. Our experiments are, to our knowledge, the first in-situ PDF studies in organic solvents with a 30 mM ethanolic solution of zinc acetate dihydrate. We find the nucleation to involve a three-step process: i) Right upon the base addition which initiates the reaction, well-known primary tetrahedral precursors Zn_4OAc_6 form and quickly assemble to 8 Å clusters with only local tetrahedral order. ii) After 60 minutes, we identify magic-sized clusters (MSC) of 1.3 nm diameter with Wurtzite structure, which subsequently build up a disordered shell that is identified in the PDF as a sinusoidal oscillation. iii) Upon reaching a critical volume, this core-shell structure transforms into 2.5 nm well-ordered nanoparticles roughly 120 min after base addition. These do not grow further. Thereafter, the Zn_4OAc_6 precursors, the 1.3 nm MSCs and the 2.5 nm particles coexist, whereby the number of 2.5 nm particles increases at the expense of the precursors and MSCs. SAXS studies confirm the continuous growth of the disordered shell as well as a bimodal size distribution with centroids at 1.4 nm and 2.2 nm. The MSC and nanoparticle sizes coincide with stable closed shells of ZnO_4 tetrahedrons in the hexagonal Wurtzite structure.

[1] Ludi, B. & Niederberger, M., *Dalton Trans.* 2003, 42, 12554

[2] Y.-J. Hu, K. E. Knope, S. Skanthakumar, *et al.*, *J. Am. Chem. Soc.* 2013, 135 (38), 14240

[3] Jensen, K. M. O.; Christensen, M., Juhas, *et al.*, *J. Am. Chem. Soc.* 2012, 134, 6785

Keywords: nanoparticle, nucleation, in-situ PDF

MS01_O4

Total scattering investigation of local structure around iron in FeV-based bcc-hydrides

Henrik Mauroy^a, Magnus H. Sørby^a, Ulrich Ulmer^b,
Maximilian Fichtner^b & Bjørn C. Hauback^a

^aInstitute for Energy Technology, Physics Department, P.O.Box 40, 2027 Kjeller, Norway

^bKarlsruhe Institute of Technology, Institute of Nanotechnology, Hermann-von-Helmholtz Platz 1, 76344 Eggenstein-Leopoldshafen, Germany
E-mail of the corresponding author: henrik.mauroy@ife.no

Hydrogen storage in solids has several advantages compared to compression of hydrogen gas, most notably higher volumetric hydrogen density and better safety. bcc-based Ti-V-M alloys (M = Cr, Mn, Fe, Co or Ni) have decent hydrogen capacities (2-3 wt.%) as well as suitable thermodynamics and kinetics for hydrogen storage purposes [1]. Vanadium is 10 times more expensive than other early transition metals, which is a severe limitation for utilization of the Ti-V-M alloys for hydrogen storage. Much cheaper ferrovandium alloys (FeV = Fe~0.2,V~0.8) can be used instead, although the reduction in price comes at the cost of lower hydrogen capacity. Kinetic and thermodynamic properties are also altered; however sometimes in a favorable way [2-4].

The crystallographic structure of Ti-FeV-M-hydrides is, on average, very simple, with the metal atoms distributed on identical sites and hydrogen in partially filled tetrahedral sites. This arrangement is highly disordered, which makes it challenging to understand structure-property relations by regular powder diffraction alone. However, in order to intelligently improve the properties of these alloys, such relations are crucial to understand.

Total scattering experiments, using either neutrons or X-rays, are powerful tools to extract information about short-range atomic order. Combining such measurements with Reverse Monte Carlo modelling (RMC) [5] and pair-distribution function (PDF) analysis, has earlier shown to work well for metal hydrides [6-8]. Such an approach has been applied to a series of bcc-based hydrides with V, Fe, Ti, Cr and/or Nb at different hydrogen loadings. The experiments were performed at ISIS (UK) using the GEM diffractometer [9], and SNBL (ESRF,France) using the newly commissioned total scattering setup [10], respectively. The results are presented with special emphasis on the local structure around Fe which is paramount to understanding the effects of substituting expensive vanadium with much cheaper ferrovandium.

Uehara, H. Ishikawa, *J. Alloys Comp.* 1997, 253, 232. [3] S.F. Santos, J. Huot, *J. Alloys Comp.* 2009, 480, 5 [4] J. Mi, F. Lü, X. Liu, L. Jiang, Z. Li, S. Wang, *Journal of Rare Earths* 2010, 28, 781. [5] R.L. McGreevy, L. Pusztai, *Molecular Simulation*. 1988, 1, 359. [6] M.H. Sørby, A. Møllergård, R. Delaplane, A. Wannberg, B.C. Hauback, H. Fjellvåg, *J. Alloys Comp.* 2004, 363, 209. [7] M.H. Sørby, *Zeitschrift für Kristallographie*. 2008, 223, 617. [8] K. Itoh, T. Shoumura, K. Mori, M. Sugiyama, T. Fukunaga, *J. Non-Cryst. Solids*. 2007, 353, 1975. [9] A.C. Hannon, *Nucl. Instrum. Meth.* 2005, A 551, 88. [10] P.M. Abdala, H. Mauroy, W. van Beek, *J. Appl. Cryst.* 2014, 47, 449.

Keywords: Total scattering, hydrogen storage, metal hydrides, neutron scattering, x-ray scattering, Reverse Monte Carlo modelling

[1] A.J. Maeland, G.G. Libowitz, J.F. Lynch, *J. Less-Com. Met.* 1984, 104, 361. [2] H. Miyamura, T. Sakai, N. Kuriyama, H. Tanaka, I.

Posters:

MS01_P1

Nano-Domain States of Perovskite-like Oxides Based on Strontium Ferrite with a High Oxygen Deficiency

Uliana V. Ancharova^a & Svetlana V. Cherepanova^b

^aInstitute of Solid State Chemistry and Mechanochemistry SB RAS, Russia,

^bBoriskov Institute of Catalysis SB RAS, Russia

e-mail: ancharova@gmail.com

Many of non-stoichiometric perovskite-like oxides $ABO_{3-\delta}$ have nano-domain structure for the values of oxygen stoichiometry $3-\delta$ close to vacancy-ordered brownmillerite phase $ABO_{2.5}$ [1-5]. Nano-domain structures appear as a result of phase separation to vacancy-ordered phases and are three-dimensional intergrowth structures of nano-sized brownmillerite domains (perpendicularly oriented to each other) in a matrix of host perovskite lattice. However, due to coherent jointing of different 90° orthorhombic domains and regularity of cation sublattice in the system the nano-domain structure appears at X-Ray diffraction patterns as narrow intense peaks of high-symmetric perovskite structure with weak broadened superstructural reflections.

This work is devoted to the structural investigations of the series of nano-structured oxides based on strontium ferrites $SrFe_{1-y}M_yO_{3-\delta}$ ($M=V;Mo$; $0<y<0.2$) with a high degree of oxygen non-stoichiometry ($2.5<3-\delta<2.7$). Using combination of synchrotron radiation X-Ray diffraction, HRTEM and Mössbauer spectroscopy a systematic analysis of the influence of M -cation and oxygen content on the nanostructure and types of disorder in the structure is held.

By computer simulation of defective structures [5] and its X-ray diffraction patterns [6] it is shown that, depending on the way of organization of the nano-domains and on the extended defects present in the structure, the resulting diffraction effects have different features. As a result of simulations a systematic analysis of the influence of different types of disorder in strongly nonstoichiometric oxides on the diffraction patterns is performed.

Comparison of calculated and experimentally obtained powder diffraction effects demonstrate that with increase in substitution degree y by high-charged cations M and with increase in oxygen stoichiometry $3-\delta$ the nano-domain system evolves towards reducing the size of the domains and complication of their internal organization.

This work was carried out with the involvement of equipment belonging to the shared research center

"SSTRC" (supported by the Ministry of Education and Science of the Russian Federation).

[1] M.A. Alario-Franco, J.C. Joubert & J.P. Lévy, *Materials Research Bulletin*. 1982, 17, 733 [2] N. Nakayama, M. Takano, S. Inamura, N. Nakanishi & K. Kosuge, *Journal of Solid State Chemistry*. 1987, 71, 403 [3] F. Lindberg, G. Svensson, S.Ya. Istomin, S.V. Aleshinskaya & E.V. Antipov, *Journal of Solid State Chemistry*. 2004, 177, 1592 [4] H. D'Hondt, J. Hadermann, A.M. Abakumov, A.S. Kalyuzhnaya, M.G. Rozova, A.A. Tsirlin, R. Nath, H. Tan, J. Verbeeck, E.V. Antipov & G.V. Tendeloo, *Journal of Solid State Chemistry*. 2009, 182, 356 [5] U.V. Ancharova & S.V. Cherepanova, *Powder Diffraction Journal*. 2013, 28, S2, S51 [6] T. Proffen & R.B. Neder, *Journal of Applied Crystallography*. 1997, 30, 171

Keywords: synchrotron radiation X-Ray diffraction, HRTEM, Mössbauer spectroscopy, nano-domain structure, non-stoichiometry, structure simulation, Debye calculations of XRD patterns, line profile analysis

MS01_P2

Total Scattering Experiment on glass and crystalline materials at the ESRF on the ID11 beamline

Andrea Bernasconi^a, Jonathan Wright^a, Gavin Vaughan^a & Nicholas Harker^a

^aEuropean Synchrotron Radiation Facility, France, e-mail: andrea.bernasconi@esrf.fr

ID11 is a multi-purpose high-energy beamline at the European Synchrotron Radiation Facility (ESRF), in Grenoble. Due to the high energy source (<140 keV) and flexible, high precision sample mounting (allowing small sample-detector distances to be achieved), experiments such as total scattering in transmission geometry are possible and allow exploration of a wide range of Q , and so providing high real space resolution.

Preliminary energy calibration was performed on two standards (CeO_2 and Si powders) at 7 different sample-detector distances, following the method of Hong et al. [1]: achieving a final calibrated wavelength of 0.1599 Å, with linear R^2 factors of 0.9999 and very small % residuals ($<$ than 0.1).

A range of samples (glasses and crystalline powders) were then measured, first putting the detector as close as possible to the sample (distance ~ 10 cm), and then moving it vertically and laterally with respect to the beam in order to have circular and quarter circle sections of diffraction rings, with consequent Q max at the edge of the detector of about 24 and 36 Å⁻¹, respectively.

All data were integrated using both packages available at the beamline (pyFAI [2] and FIT2D [3]) and then

normalized and corrected with GudrunX [4], and PDFGetX3 [5].

These results are compared to see the effects of Q-range and statistics on the PDF's of the different samples.

[1] X. Hong et al., *Review of Scientific Instruments*, 2012, 83, 063901
[2] J. Kieffer et al., *Powder Diffraction*, 2013, 28, 339 [3] A. P. Hammersley, FIT2D: An Introduction and Overview, 1997 [4] A.K. Soper, GudrunN and GudrunX: Programs for Correcting Raw Neutron and X-ray Diffraction Data to Differential Scattering Cross Section, 2010 [5] P. Juhas et al., *Journal of Applied Crystallography*, 2013, 46, 560.

Keywords: total scattering, data treatment

MS01_P3

DebUsSy 2.0 - the new release of a Debye User System for nanocrystalline and/or disordered materials

[Antonio Cervellino](#)^a, [Antonietta Guagliardi](#)^b, [Ruggero Frison](#)^b & [Federica Bertolotti](#)^c

^aPaul Scherrer Institut, Villigen, Switzerland

^bIstituto di Cristallografia, CNR, Como, Italy

^cUniversità dell'Insubria, Como, Italy.

antonio.cervellino@psi.ch

The theoretical understanding of materials properties strongly depends on the knowledge of the material's atomic structure and, at the nanoscale, also of particle size, shape, strain and their distributions and interrelations. Diffraction patterns of disordered, defective or simply nanosized samples typically present broad and continuous intensity distribution not easily dealt with by conventional crystallographic techniques. Debye's scattering equation [1] provides directly the elastic differential cross section, or the powder diffraction pattern. Its input information is the set of atomic positions, or more precisely, the interatomic distances distribution. It does not require periodicity and order. As such, it comes as a powerful tool for quantitatively determining the structural properties of disordered and nanostructured materials. DebUsSy [2] is a suite of programs implementing the Debye equation for the analysis of powder diffraction data from nanocrystalline, defective and/or non-periodic materials. It has been successfully applied on several nanomaterials (metals, alloys, oxides, bioceramics, molecular drugs and metal-organic compounds) [3-5]. It has the in-built capability to deal with size/shape distributions of nanocrystal families, and it has the unique capability to explicitly deal with the size/shape dependence of other microstructural parameters (lattice parameter, thermal vibration amplitudes, site occupancy

and stoichiometry). DebUsSy uses a two-step approach: I) building databases of efficiently encoded interatomic distances; II) calculation of the diffraction patterns and optimization of model parameters vs the experimental data by means of the DebUsSy main program. The 2.0 release of DebUsSy has been extended with different optimization algorithms and with many flexible tools to build nanocrystal families with different shape, size and defect distributions. A Graphical User Interface makes easy to run any of the programs within the Suite and to display the results. A set of satellite programs for managing and correcting the experimental data is added. Fondazione Cariplo's support is gratefully acknowledged (project 2011-0289).

[1] P. Debye, *Phys. Z.* 1915 31, 797-798.

[2] A. Cervellino, C. Giannini, A. Guagliardi, *J. Appl. Cryst.* 2010, 43, 1543; A. Cervellino, R. Frison, F. Bertolotti, A. Guagliardi, 2014, *in preparation*.

[3] A. Cervellino, A. Maspero, N. Masciocchi, A. Guagliardi, *Cryst. Growth. Des.* 2012, 12, 3631.

[4] J.M. Delgado-Lopez, R. Frison, A. Cervellino, J. Gomez-Morales, A. Guagliardi, N. Masciocchi. *Adv. Funct. Mat.* 2014, 24, 1090.

[5] R. Frison, G. Cernuto, A. Cervellino, O. Zaharko, G. M. Colonna, A. Guagliardi, N. Masciocchi. *Chem. Mater.* 2013, 25, 4820

Keywords: Debye method, nanocrystalline materials, Total scattering

MS01_P4

XPDF: A Dedicated X-ray Pair Distribution Function Beamline at Diamond Light Source

[Philip A. Chater](#)^a, [Matthew G. Tucker](#)^{a,b}, [John P. Sutter](#)^a, [Michael Hillman](#)^a & [Heribert Wilhelm](#)^a

^aDiamond Light Source, Harwell Campus, Didcot, Oxfordshire, OX11 0DE, UK, e-mail: xpdf@diamond.ac.uk

^bISIS Facility, Harwell Campus, Didcot, Oxfordshire, OX11 0QX, UK.

The importance of understanding local structure is becoming increasingly apparent in diverse disciplines such as materials chemistry, solid-state physics, earth sciences and pharmaceuticals. The pair distribution function (PDF) technique provides a quantitative probe of the local correlations in materials, and as such can be used to drive the refinement of local structure models.

PDF measurements are the primary approach for understanding the atomic structure of glasses and fluids [1]. However, the PDF method can be applied to both non-crystalline and crystalline methods alike; it is increasingly being used to provide a unique insight into the properties of crystalline materials as well [2].

XPDF will be a new, independent side-station to the Extreme Conditions beamline I15 at Diamond Light Source. It will be committed to the fast and reliable production of PDF data, and will be the first dedicated X-ray PDF beamline in Europe. The design of XPDF allows for rapid data collection with Q_{\max} of up to 41 \AA^{-1} , giving a real space resolution of $\approx 0.15 \text{ \AA}$.

Here we present an outline of the XPDF beamline and simulations of its performance. The optics, a horizontally focusing Laue monochromator and a vertically focusing multi-layer mirror, have been designed to deliver maximum flux to the sample position. Large area detectors will be used in different configurations to either provide maximum Q coverage, or simultaneously collect medium resolution Bragg and PDF data for total scattering studies. The sample station will initially accommodate high throughput and variable temperature experiments, with more complex environments to be developed at a later stage. XPDF is scheduled to receive its first users in June 2016.

[1] C. J. Benmore, *ISRN Materials Science*. 2012, 852905 [2] C. A. Young and A. L. Goodwin, *J. Mater. Chem.* 2011, 21, 6464.

Keywords: pair distribution function, total scattering, synchrotron, beamline

MS01_P5

Modeling Nano- and Mesoscale Disorder in Yttrium-Doped Ceria by XRPD-NPD Pair Distribution Function

Stefano Checchia^a, Marco Scavini^{a,b}, Paolo Masala^a, Michela Brunelli^a, Claudio Ferrero^c & Mauro Coduri^{a,d}

^aUniversità degli Studi di Milano, Italy, e-mail: stefano.checchia@unimi.it

^bISTM-CNR and INSTM Unit, Milano, Italy

^cEuropean Synchrotron Radiation Facility, Grenoble, France

^dENI-CNR, Lecco, Italy

Cerium oxide (CeO_2) forms a continuous range of solid solutions with Y_2O_3 . Upon Ce^{4+} substitution with Y^{3+} , half an oxygen vacancy is created. Are these defects randomly scattered in the structure or are they ordered? Answers are needed for rationalizing the ion-conducting behavior of doped ceria from a structural point of view and, thus, making suitable SOFC electrolytes out of such materials.

In this work, doping-dependence of charge transport in Y-doped ceria was explained by thorough investigation of its defect structure and, thereby, a method for obtaining nanodomain size from the refinement of PDF parameters was consistently applied. Combining reciprocal-space and real-space (PDF) analysis allowed

mapping the structure evolution of the whole $\text{Ce}_{1-x}\text{Y}_x\text{O}_{2-x/2}$ system over three length scales: i) average; ii) mesoscopic ($10\text{-}100 \text{ \AA}$) and iii) local ($<10 \text{ \AA}$).

XRPD-NPD investigations were performed at the ID31 beamline at the ESRF and at the D20 and D4c instruments at ILL, Grenoble. By increasing Y concentration, the average structure evolves from the fluorite structure of CeO_2 to the C-type of Y_2O_3 . Static disorder increases with Y-doping from the fluorite-like region up to a maximum around $x=0.4$, as displayed by *msd* parameters.[1] Reciprocal-space analysis on compositions in the $0.250 < x < 0.438$ interval revealed presence of broad superstructure peaks, sharpening upon Y-doping, which are accounted for by anti-phase boundaries between Y-rich domains.[2] Domain size (10 to 40 nm) was obtained by a PDF approach based on the refinement of structural parameters centering on different r distances. On the atomic scale, PDF showed that Ce and Y ions preserve the very environment they have in the corresponding pure oxides. C-type interatomic distances, mapped throughout the composition range, suggest an oxygen relaxation mechanism towards vacancies taking place. Accordingly, a *biphasic* model involving Y_2O_3 -like domains at low doping is proposed.[2]

[1] Coduri, M., Scavini, M., Allieta, M., Brunelli, M., Ferrero, C., *Chemistry of Materials*. 2013, 25, 4278

[2] Coduri, M., Scavini, M., Allieta, M., Brunelli, M., Ferrero, C., *Journal of Physics: Conference Series*. 2012, 340, 012056

Keywords: pair distribution function, synchrotron x-ray powder diffraction, neutron powder diffraction, nano-domains, disordered oxides, solid oxide fuel cells

MS01_P6

Nuclear Enhanced X-ray Maximum Entropy Method Used to Analyze Local Distortions in Simple Structures

Sebastian Christensen^a, Niels Bindzus^a, Mogens Christensen^a & Bo Brummerstedt Iversen^a

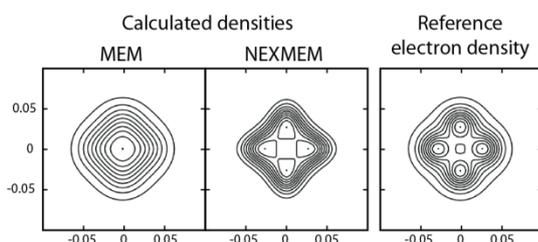
^aAarhus University, Denmark, e-mail: sebastian@chem.au.dk

We introduce a novel method for reconstructing pseudo nuclear density distributions (NDDs): Nuclear Enhanced X-ray Maximum Entropy Method (NEXMEM). NEXMEM offers an alternative route to experimental NDDs, exploiting the superior quality of synchrotron X-ray data compared to neutron data.

The method was conceived to analyse local distortions in the thermoelectric lead chalcogenides, PbX ($X = \text{S},$

Se, Te). Their extraordinary thermoelectric performance has caused huge research activity, but the mechanisms governing their unexpected low thermal conductivity still remain a controversial topic. It has been proposed to result from anharmonic phonon scattering or from local fluctuating dipoles on the Pb site.[1,2] No macroscopic symmetry change are associated with these effects, rendering them invisible to conventional crystallographic techniques. For this reason PbX was until recently believed to adopt the ideal, undistorted rock-salt structure. NEXMEM employs a simple procedure to normalize extracted structure factors to the atomic form factors. The NDD is reconstructed by performing maximum entropy calculations on the normalized structure factors.

NEXMEM has been validated by testing against simulated powder diffraction data of PbTe with known displacements of Pb. The increased resolution of NEXMEM proved essential for resolving Pb-displacement of 0.2 Å in simulated data. The figure below shows Pb in the (100) plane for calculated MEM and NEXMEM densities, as well as the reference electron density. In addition, we have applied NEXMEM to multi-temperature synchrotron powder X-ray diffraction collected on PbX. Based on powder diffraction data, our study demonstrates that NEXMEM successfully improves the atomic resolution over standard MEM. This new tool aids our understanding of the local distortions present in PbX. In the future it may be used for widespread characterization of subtle atomic features in crystals with unusual properties.



[1] E. S. Bozin et al., *Science*, 2010, 330, 1660-1663

[2] O. Delaire et al., *Nature Materials*, 2011, 10, 614-619

Keywords: Maximum Entropy, Disorder, Powder X-ray Diffraction, Thermoelectric Materials

A comparison of total scattering data from various sources: the case of a nanometric spinel

Giorgia Confalonieri^a, Monica Dapiaggi^a, Marco Sommariva^b, Milen Gateshki^b, Andy N. Fitch^c & Simon J.A. Kimber^c

^aUniversity of Milan, Italy, e-mail: giorgia.confalonieri@unimi.it

^bPANalytical BV, The Netherlands

^cESRF, France

Nanocrystalline spinel gahnite (ZnAl_2O_4 , 2-3 nm) has been measured with three different instruments: (i) ID31 high resolution diffractometer at the ESRF (9 line detectors, all with crystal analyzers, $Q_{\text{max}}=22 \text{ \AA}^{-1}$), (ii) ID15B high energy beamline at the ESRF with 2D image plate detector ($Q_{\text{max}}=32 \text{ \AA}^{-1}$), (iii) PANalytical diffractometer with silver $K\alpha$, with an X'Celerator detector ($Q_{\text{max}}=20.5 \text{ \AA}^{-1}$). The Pair Distribution Functions (PDFs) were obtained with PDFgetX3 [1], by subtracting the relevant empty capillary scattering, and correcting and normalizing the data. The same procedure was applied to all data sets. The diffraction geometries and the wavelengths of the incident X-rays were chosen in order to make the comparison as comprehensive as possible, and the material under analysis was chosen for its nanometric (and possibly disordered) nature, to give rise to a challenge for all the diffractometers involved. None of the latter should have a clear advantage: for instance, even the large resolution, in the direct space, of ID15B is not enough to resolve the very small difference between Zn-O and Al-O bonds in the first PDF peak; besides the material is nanometric (about 2-3 nm), so the very high resolution of ID31 does not bring a clear benefit to its PDF, if we disregard its smaller Q_{damp} , (i.e. a gentler function envelop at high r). The PDF and $F(Q)$ functions were visually compared, and then the three PDFs were refined by means of PDFgui [2], using the simplest possible model of a spinel (totally direct, with space group symmetry respected). All the refinements were made exactly in the same way, by refining the same parameters, for the sake of a fair comparison. Small differences could be highlighted in the results, and all the data sets were perfectly and easily refinable. Differences in the refined parameters could also be detected on PDFs obtained with a different procedure for background subtraction, so attention should be paid to the procedure of PDF attainment from total scattering data.

[1] P. Juhás, T. Davis, C.L. Farrow and S.J.L. Billinge, *J. Appl. Cryst.* 2013, 46, 560 [2] C.L. Farrow, P. Juhás, J.W. Liu, D. Bryndin, E.S. Božin, J. Bloch, Th. Proffen and S.J.L. Billinge, *J. Phys.: Condens. Matter.* 2007, 19, 335219

Keywords: PDF, total scattering, nanomaterials, synchrotron, in-house diffractometer

MS01_P8

Total Scattering Studies of Disordered Bi-Fe-Mn Pyrochlore Oxides from Hydrothermal Synthesis

Luke M. Daniels^a, Richard I. Walton^a & Alex C. Hannon^b

^aDepartment of Chemistry, University of Warwick, Coventry, UK, CV4 7AL.
^bISIS Facility, Rutherford Appleton Laboratory, Harwell, Oxford, OX11 0QX

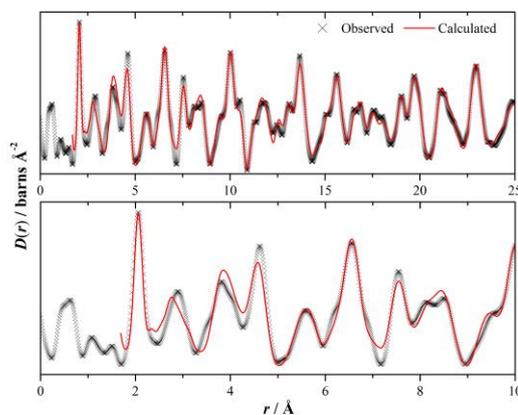
Mixed-metal pyrochlore oxides receive increased amounts of attention for their diverse range of properties including: fast oxide-ion conductivity for solid oxide fuel cells, ferroelectricity, superconductivity, frustrated magnetism, and optics [1]. The $A_2B_2O_6O'$ pyrochlore structure is a system well known for its potential to accommodate various types of structural disorder. These can take the form of a deficient A site, mixing of metals across both A and B sites, whilst there is flexibility in the O' site through partial occupation, or various other species such as hydroxide, halides, or water occupying the anion sites [2]. Further disorder can be introduced depending upon the metals present. The stereochemically active electrons on lone-pair ions such as Bi^{3+} and Pb^{2+} can induce static displacements into the A site cation sub lattice, which results in further disorder of the coordinating oxide ions [3]. These forms of disorder will often affect the structure of the material on a local scale, not evident when using traditional diffraction techniques.

Pair distribution function (PDF) analysis of total scattering data has proved its worth as an ideal technique for the study of disordered pyrochlores, with previous work showing it is necessary to understand their local structures as these details are not shown in the analysis of Bragg scattering [4]. For example, in $Bi_2Ti_2O_7$ and $Bi_2Ru_2O_7$, analysis of the PDF data shows that the bismuth cation is off-centre from its ideal crystallographic position and that the O' partially occupies two separate sites [5-6].

We present a total scattering study of two new metastable Bi-Fe-Mn pyrochlore oxides produced through low-temperature hydrothermal synthesis. These materials display low-temperature spin-glass type frustrated magnetic behaviour.

The refinement of long-range structure against Bragg data shows that the bismuth is mixed across both the A and B sites in compositions of $(Na_{0.82}Bi_{1.18})(Fe_{0.93}Mn_{0.25}Bi_{0.82})O_{6.13}$ and $(K_{0.85}Bi_{1.15})(Fe_{1.09}Mn_{0.15}Bi_{0.85})O_{6.21}$. It is confirmed through X-ray absorption near edge spectroscopy (XANES) that both Bi^{5+} and Bi^{3+} are present, with the latter, being larger, residing on the A site. Total neutron scattering data were collected on the GEM diffractometer at ISIS, the U.K. spallation neutron

source. Modelling these systems using the ideal pyrochlore structure yields a poor fit to the PDF data on the local scale ($<8.5 \text{ \AA}$) but improves with increasing r ; indicating a degree of local structural disorder. Enhancements to the fit can be made using Bi^{3+} and oxide ions that are displaced off-centre from their ideal positions accounting for this local disorder.



Fit to PDF data of $(Na_{0.82}Bi_{1.18})(Fe_{0.93}Mn_{0.25}Bi_{0.82})O_{6.13}$ (upper) highlighting local structural disorder in low r region (lower).

[1] M. T. Weller *et al*, *Dalton Trans.* 2004, 19, 3032 [2] M. A. Subramanian *et al*, *Prog. Solid State Chem.* 1983, 15, 55 [3] Q. Zhou *et al*, *J. Alloys Compd.* 2014, 589, 425 [4] H. Y. Playford *et al*, *Chem. Mater.* 2011, 23, 5464 [5] A. L. Hector *et al*, *J. Solid State Chem.* 2004, 177, 139 [6] D. P. Shoemaker, *Phys. Rev. B* 2011, 84, 064117.

Keywords: Total Scattering, Pair Distribution Function, Pyrochlore, Disorder, Hydrothermal

MS01_P9

Studying Morphotropic Phase Boundary through Total Scattering Technique

Kaustuv Datta & Reinhard B. Neder

Lehrstuhl für Kristallographie und Strukturphysik, Friedrich-Alexander-Universität Erlangen-Nürnberg Erlangen, Germany, e-mail: Kaustuv.Datta@physik.uni-erlangen.de

Morphotropic phase boundary (MPB) is an important theme in the research of ferroelectric materials since materials often exhibit enhanced physical properties at MPB. Although an established understanding of creating MPB behaviour relies on invoking instability of average crystal structure or a low-symmetry monoclinic phase in the system driven by composition [1], the actual mechanism is far more complex and heavily dependent on the local ordering of the cations as

evidences found in recent diffuse scattering studies^[2] on either lead-free or lead-based systems.

We have studied an important and popular ferroelectric system $x\text{BiScO}_3-(1-x)\text{PbTiO}_3$, which was first reported in 2001 with MPB characteristics^[3], through total scattering technique to understand its structural evolution as a function of composition in the vicinity of the MPB. Total scattering technique which is essentially the analysis of the pair distribution function (PDF) of a system provides crucial structural information at the microscopic level which are not easily available from conventional structural analysis like Rietveld refinement. Both x-ray and neutron powder diffraction experiments were carried out on six different compositions of BS-PT in the range $0.30 < x < 0.40$ and neutron PDFs were analysed through RMC simulations to extract the behaviour of individual cations. It was observed that locally there was no abrupt change in any of the cation-cation correlations to assign the MPB unambiguously, however, a trend was noticed in the sigmas of individual cationic displacements where the reported MPB composition shows a minimum.

[1] R. Guo, L. E. Cross, S-E. Park, B. Noheda, D. E. Cox, G Shirane *Phys. Rev. Lett.* 2000, **84**, 5423.

[2] R. E. Eitel, C. A. Randall, T. R. Shrout, P. W. Rehrig, W. Hackenberger, S -E Park, *Jpn. J. Appl. Phys.* 2001, **40**, 5999.

[6] D. J. Goossens, *ISRN Materials Science*, 2013, **2013**, 107178.

Keywords: pair distribution function, local structure, ferroelectric materials, morphotropic phase boundary

MS01_P10

Evidence for a domain structured model of amorphous silicates from X-ray total scattering measurements.

[Sarah J. Day^a](#), [Stephen P. Thompson^a](#) & [Aneurin Evans^b](#)

^aDiamond Light Source, Oxfordshire, UK

^bKeele University, Staffordshire, UK
e-mail: sarah.day@diamond.ac.uk

Total Scattering (TS) measurements have been obtained for amorphous silicates of varying composition (Fe,Mg,Ca), produced via a sol-gel method, across a range of temperatures (300, 600, 900K) using beamlines I12 and I15 at the Diamond Light Source, UK. Amorphous silicate materials have been studied in great detail in an attempt to understand their structural nature, however a definite structural model has not yet been determined.

Currently there are two competing structural models that are believed to best represent the structure of amorphous silicates. The Zachariasen-Warren model [1,2] suggests that Si-O tetrahedra are linked together in a statistically disordered way to form a continuous random network, having no significant long-range periodicity, while conversely the microcrystal model [3,4,5] suggests a continuous statistically random network that provides links between the surfaces of ultrafine microcrystalline regions (~15-20Å) forming a domain structured material [6].

Through pair distribution function analysis of TS data we observe that at a temperature of 600°C, the range over which the amorphous silicate exhibits structural order is reduced from 30Å to ~15Å. This is believed to be due to the loss of bonded hydroxyls between randomly orientated silicate domains [7]. The remaining silicate structure at distances of <15 Å remains stable however, and no changes are observed in terms of the shape or position of the peaks.

These results, therefore, provide additional evidence to support the microcrystal model, suggesting that the amorphous silicate structure can be well described well by a microcrystalline domain structure. We find that this is true for a range of amorphous silicate compositions, including those of FeSiO_3 , MgSiO_3 , CaSiO_3 and combinations of these.

[1] Zachariasen W. H., 1932, *J. Am. Ceramic Soc.*, 17, 3841 [2]

Warren B. E., 1933, *Z. Kristallographie*, 86, 349

[3] Lebediev A. A., 1921, *Trans. Opt. Inst. Petr.*, 2, 10

[4] Randall J. T., Rooksby H. P., Cooper B. S., 1930, *J. Soc. Glass Tech.*, 14, 219

[5] Valenkow N., Porai-Koshitz E., 1936, *Z. Krist.*, 95, 195

[6] Verweij H., Konijnendijk W. L., 1976, *J. Am. Ceramic Soc.*, 59, 517

[7] Thompson S. P., Parker J. E. & Tang C.C. 2012, *Astron. & Astrophys.* 545, 60

Keywords: Amorphous silicates, Total Scattering, Pair-Distribution Function.

MS01_P11

Reverse Monte Carlo refinement of a layered double hydroxide nanosheet

[N. P. Funnell^a](#), [Q. Wang^b](#), [L. Connor^c](#), [M. G. Tucker^d](#), [D. O'Hare^a](#) & [A. L. Goodwin^a](#)

^aUniversity of Oxford, UK

^bBeijing Forestry University, China

^cDiamond Light Source, Harwell Science and Innovation Campus, UK

^dISIS Facility, Harwell Science and Innovation Campus, UK,

e-mail: nicholas.funnell@chem.ox.ac.uk

Layered double hydroxides (LDHs) are among some of the most chemically versatile materials, finding use in CO₂ absorption, flame retardation and drug delivery [1]. A recent advance in the chemistry of LDHs has been the development of a new synthetic route to obtaining highly-dispersed, delaminated nanosheets that remain exfoliated on drying [2].

The high surface area (*ca* 450 m²g⁻¹) of these new ultra-thin LDH phases is anticipated to give rise to superior performance, relative to 'bulk' LDH forms. However, the challenge presented by these materials, and indeed by all nanosheets, is that structural characterisation is complicated by the absence of long-range, three-dimensional periodicity, precluding the use of conventional crystallographic approaches.

We report the extension of the reverse Monte Carlo technique [3,4] to enable structural refinement of two-dimensional nanomaterials. By fitting an atomistic model to both real and reciprocal space data, we are able to look at local-scale geometry and also longer-range correlations, such as cation distribution within the sheet, which is thought to play an influential role in LDH functionality.

-
- [1] Q. Wang and D. O'Hare, *Chem. Rev.*, 2012, 112, 4124 [2] Q. Wang and D. O'Hare, *Chem. Commun.*, 2013, 49 6301
[3] M. G. Tucker, D. A. Keen, M. T. Dove, A. L. Goodwin and Q. Hui, *J. Phys.: Condens. Matter*, 2007, 19, 335218
[4] N. P. Funnell, Q. Wang, L. Connor, M. G. Tucker, D. O'Hare and A. L. Goodwin, *manuscript submitted*

Keywords: Layered double hydroxide, nanosheet, total scattering, reverse Monte Carlo

MS01_P12

PDF Analysis on a Laboratory Diffractometer: Adapting the Experiment to the Specifics of the Material

[Milén Gateshki](#), Céleste A. Reiss & Marco Sommariva

PANalytical B.V., The Netherlands, e-mail: milen.gateshki@PANalytical.com

The increased interest in recent years regarding the properties and applications of nanomaterials has also created the need to characterize the structures of these materials. However, due to the lack of long-range atomic ordering, the structures of nanostructured and amorphous materials are not accessible by conventional diffraction methods used to study crystalline materials. One of the most promising techniques to study nanostructures using X-ray diffraction is by using the total scattering (Bragg peaks and diffuse scattering) from the samples and the pair distribution function

(PDF) analysis. The pair distribution function provides the probability of finding atoms separated by a certain distance. This function is not direction-dependent; it only looks at the absolute value of the distance between the nearest neighbors, the next nearest neighbors and so on. The method can therefore also be used to analyze non-crystalline materials. From experimental point of view a typical PDF analysis requires the use of intense high-energy X-ray radiation ($E \geq 15$ KeV) and a wide 2θ range.

After the initial feasibility studies regarding the use of standard laboratory diffraction equipment for PDF analysis [1-3] this application has been further developed to achieve improved data quality and to extend the range of materials, environmental conditions and geometrical configurations that can be used for PDF experiments. Studies performed on different nanocrystalline and amorphous materials of scientific and technological interest, including organic substances, oxides, metallic alloys, etc. have demonstrated that PDF analysis with a laboratory diffractometer can be a valuable tool for structural characterization of nanomaterials. This contribution presents several examples of laboratory PDF studies, in which the experimental conditions have been successfully adapted to match the specific requirements of the materials under investigation.

-
- [1] J. te Nijenhuis, M. Gateshki, M. J. Fransen, *Z. Kristallogr. Suppl.* 2009, 30, 163. [2] C. A. Reiss, A. Kharchenko, M. Gateshki, *Z. Kristallogr.* 2012, 227, 257. [3] M. Sommariva, *Solid State Phenomena* 2013, 203-204, 17.

MS01_P13

PDF calculations from low- and high-temperature data using a Stoe Stadi P with Ag K α_1 -radiation and a Dectris MYTHEN 1K detector

[Thomas Hartmann](#)^a & [Lothar Fink](#)^b

^a *Stoe & Cie GmbH, Darmstadt, Germany, hartmann@stoe.com*
^b *Goethe University, Frankfurt, Institute for Inorganic and Analytical Chemistry, Frankfurt, Germany, fink@chemie.uni-frankfurt.de*

An impressive comparison of $G(r)$ calculated with PDFgetX2⁽¹⁾ from data of Naphthalen taken at room temperature with a Stoe Stadi P powder diffractometer in Transmission mode equipped with a Ag-tube, a Ge(111)-monochromator for pure Ag-K α_1 -radiation (0.5594 Å) as well as the Dectris MYTHEN 1K with 1mm sensor thickness and from synchrotron data,

beamline X17A, NSLS Brookhaven with a wavelength of 0.1839 Å, yields amazingly similar peak widths for both experiment sites.

To observe the temperature dependence of this resolution, the same laboratory setup with an additional Oxford Cryosystems Cobra or a Stoe furnace has been chosen to compare the signal width as a function of T.

Low temperature data for these PDF calculation experiments has been taken from LaB₆ as a crystalline standard and Naphthalene as well known organic phase as well as data from some semi-crystalline or amorphous carbon phases. In addition high temperature G(r)-data from Ammonium Nitride will be demonstrated.

[1] Qiu, X., Thompson, J.W. and Billinge, S.J.L., J. Appl. Chem., (2004), 37, 678.

Keywords: PDF calculation, total scattering techniques, diffractometer, Ag-radiation, low temperature, high temperature

MS01_P14

The X-ray Total Scattering Science Program/capabilities at the Photon Sciences Department at Brookhaven National Laboratory

[A. M. Milinda Abeykoon](#)^a, Simon J. L. Billinge^{a,b} & Eric Dooryhee^a

^aBrookhaven National Laboratory, USA, e-mail: aabeykoon@bnl.gov

^bApplied Physics and Applied Mathematics Department, Columbia University

Complex properties of many technologically important materials are governed by their local structural correlations. Studying the local structure-property relationship is the key to understand and manipulate structures of these materials to improve the performance of their applications. The Atomic Pair Distribution Function (PDF) is one of the few available techniques, which can be used to study local and nanoscale fluctuations of these materials to investigate how they impact their interesting physical properties. We will present our current X-ray PDF science program and efforts to build new instrumentation at the Photon Sciences Department (PSD) at Brookhaven National Laboratory (BNL) along with some case studies to illustrate our experimental setups and sample environments. Case studies will include characterizing fluctuating charge states in two transition metal oxides using local structure as a probe. We will discuss results from two model systems, La_{1.67}Sr_{0.33}NiO₄ and LiRh₂O₄,

which can greatly benefit from our current PDF experimental capabilities.

Currently, we are in the process of building the first dedicated general user PDF beamline at the US east cost. Beamline 28-ID-B at the third generation synchrotron light source, NSLSII will use extremely high flux X-rays from a damping wiggler source. A prototype end-station for 28-ID-B is currently being tested and developed at the D&I beamline, X17A at the NSLS I. There are 8 BNL, 2 industrial and 5 university research groups are participating in this effort at X17A. We will also present the project timeline, expected day one science/user capabilities, proposed science/user programs and matured scope of the beamline, 28-ID-B.

Keywords: Total-scattering, PDF.

MS01_P15

In situ Total Scattering Study of WO₃ Nanoparticle under Hydrothermal Condition

[Dipankar Saha](#)^a, Kirsten M. Ø. Jensen^a, Christoffer Tyrsted^a, Espen D. Bøjesen^a, Aref Hasen Mamakhel^a, Ann-Christin Dippel^b, Mogens Christensen^a & Bo B. Iversen^a

^aCenter for Materials Crystallography, Department of Chemistry and iNANO, University of Aarhus, Denmark

^bDeutsches Elektronen-Synchrotron DESY, Hamburg, Germany, e-mail: dipankar@chem.au.dk

In situ total scattering studies in combination with pair distribution function(PDF) and powder X-ray diffraction (PXRD) have been used to unravel the mechanism of WO₃ nano particle formation from aqueous precursor solution ammonium metatungstate (NH₄)₆H₂W₁₂O₄₀· xH₂O (AMT) under hydrothermal condition. Total scattering studies can extract precise atomic scale structural information from solutions, amorphous solids, nanosized structures as well as from crystals [1]. Therefore, it can give information about the short and long range ordering. The reaction mechanism was followed in an *in situ* reactor at synchrotron [2]. The study reveals that a complex precursor structure exists in the solution. It consists of edge and corner sharing WO₆ octahedra. While heating the solution, precursor structure undergoes a reorientation with time converting the edge sharing octahedra to corner sharing octahedra before forming the nanoparticle. While WO₆ octahedra locally become reoriented there is no evidence of long range order. After 10 min. of heating, the nuclei in the solution abruptly cluster together and form crystalline particles. The sudden formation of

nano crystals is also confirmed by in situ PXRD measurement. Further PDF analysis also reveals that local structure in hexagonal WO_3 is different than the average structure and it also rationalizes the formation of two different hexagonal phase of WO_3 [3].

-
- [1] S. J. L. Billinge, M. G. Kanatzidis, *Chem. Commun. (Cambridge, U. K.)* 2004, 749-760.
[2] J. Becker, M. Bremholm, C. Tyrsted, B. Pauw, K. M. O. Jensen, J. Eltzholt, M. Christensen, B. B. Iversen, *J. Appl. Crystallogr.* 2010, 43, 729-736.
[3] D. Saha, K. M. Ø. Jensen, C. Trysted, E. D. Bøjesen, A. H. Mamakhel, A. C. Dippel, M. Christensen, B. B. Iversen, *Angew. Chem.* 2014, DOI: 10.1002/anie.201311254.

Keywords: hydrothermal synthesis; nanoparticles; pair distribution functions; powder X-ray diffraction

MS01_P16

NanoPDF - the computer program to simulate and analyze the Pair Distribution Function of nanocrystals

[Kazimierz Skrobas](#), Stanislaw Gierlotka, Bogdan Palosz & Svetlana Stel'makh

*Institute of High Pressure Physics, Polish Academy of Sciences, Poland,
kskrobas@unipress.waw.pl*

NanoPDF creates an atomistic model of a nanoparticle and for such a model calculates X-Ray or neutron powder diffraction pattern, structure function $S(Q)$ and, by a Fourier transform of the latter, pair distribution function $G(r)$. Cubic or hcp-type mono- and bi-atomic lattices may be build. The available crystal shapes are spheres, disks, rods and hexagonal prisms. The models created may be inspected after calling an external molecular visualization program. The model size is in principle limited only by the size of the computer memory available, the practical limit being approx. 500 000 atoms i.e. 20 nm sphere. The static nanocrystal models can be made more realistic by applying thermal displacement of atoms and introducing a series of spherical shells with altering lattice parameter to model atomic density waves introduced in [1]. The simulation part of NanoPDF is well suited for educational purposes e.g. demonstrating effect of the crystal size and shape on the diffraction pattern or the effect of the Q-range of the diffraction data on the resolution of $G(r)$. The analytical part of the program takes experimental $G(r)$ or alternatively Fourier transforms experimental $S(Q)$, and fits it with an analytical form of $G(r)$. The software can determine average lattice parameter and peak broadening of $G(r)$ or follow the changes of both along the distance scale by analyzing $G(r)$ within

narrow r-intervals. Those changes can be understood in terms of thermal motions and atomic density waves present in the nanocrystals. NanoPDF is a MS Windows™ application. It is entirely controlled from the graphical user interface and features a set of dedicated graphic routines. Those make it easy and convenient to immediately display and examine the results of the calculations performed.

-
- [1] B. Palosz, E. Grzanka, S. Gierlotka and S. Stelmakh, *Z. Kristallographie*, 2010, 225, 588

Keywords: nanocrystals, pair distribution function, atomic density waves

MS01_P17

Investigation of Orbital Disorder in Ca-doped LaMnO_3

[Peter M. M. Thygesen](#)^a, Callum A. Young^a, Midori A. Patino^a, Leigh D. Connor^b, Thomas E. Proffen^c, Matthew G. Tucker^d, David A. Keen^d, Michael A. Hayward^a & Andrew L. Goodwin^a

^a*Department of Chemistry, University of Oxford, South Parks Road, Oxford, OX1 3QR, U. K.*

^b*Diamond Light Source, Harwell Science and Innovation Campus, Didcot, U.K.;*

^c*Oak Ridge National Laboratory, Oak Ridge, TN 37831-6475, U.S.A.; dISIS Facility, STFC Rutherford Appleton Laboratory, Didcot, U. K.
e-mail: peter.thygesen@chem.ox.ac.uk*

Studies of materials that exhibit colossal magnetoresistance (CMR) have been well documented over the past decade [1]. $\text{La}_{1-x}\text{Ca}_x\text{MnO}_3$ is one such CMR material that has attracted significant attention as it is relatively cheap and straightforward to synthesize. CMR materials have potential use among the next generation of magnetic memory devices, magnetic-field sensors, and transistors. For that to be possible a clear understanding has to be determined for the origin of the CMR phenomenon.

Recent studies of CMR manganites have shown that a 'polaron glass' phase precedes CMR behaviour at high temperatures [2]. This glasslike state sits midway between the high-temperature polaron liquid and the fully orbital-ordered solid with polarons. The polarons are localized charge density fluctuations associated with lattice deformation which gives rise to static, short-range correlations. At low temperature these polaron correlations are thought to evolve into the nanoscale polarons responsible for CMR itself.

This poster describes our reasoning for the anticipated connection between the orbital disorder and CMR in

La_{1-x}Ca_xMnO₃ revealed via reverse Monte Carlo modelling of X-ray and neutron total scattering data.

[1] C Felser et al., *Angew. Chem. Int. Ed.* 2007, 46,668-699 [2] J W Lynn et al., *Phys Rev B* 2007, 76, 014437

Keywords: Disordered materials, Reverse Monte-Carlo.

MS01_P18

Quantification of stacking disordered Si-Al layer silicates by the Rietveld method for the exploration of gold deposits

[Kristian Ufer](#)^a, [Reinhard Kleeberg](#)^b & [Thomas Monecke](#)^c

^aFederal Institute for Geosciences and Natural Resources, Germany, e-mail: Kristian.Ufer@bgr.de

^bTU Bergakademie Freiberg, Germany

^cColorado School of Mines, USA

The Lagunas Norte epithermal gold deposit in the Alto Chicama region of Peru represents the largest greenfields discovery made by the gold industry in the past decade. Discovery of the deposit can be attributed to the identification of elevated gold values in stream sediments and the recognition of extensive zones of intense hydrothermal alteration caused by the interaction of the host rocks with highly acidic hydrothermal fluids. To identify mineralogical gradients that could be used as vectors to ore at Lagunas Norte and similar high-sulfidation deposits, it is critical to quantitatively determine the mineralogical composition of the variably altered host rocks, which contain disordered Si-Al layer silicates as alteration products.

Minerals like the 1:1 layer silicate kaolinite, Al₄Si₄O₁₀(OH)₈ or the 2:1 layer silicate pyrophyllite, Al₂Si₄O₁₀(OH)₂ occur in a wide variability of disorder, mainly caused by faults in layer stacking. The types of disorder have been well investigated by modeling of diffraction patterns. The models commonly used for simulations consist in different stacking of layers having vacant B or C octahedral sites (kaolinite [1]) or different translation directions of identically oriented layers (pyrophyllite [2]).

These stacking models have been adapted for a recursive structure factor calculation [3] within the description language of the Rietveld program BGMN [4]. This approach has been found to be suitable for the successful fitting of diffraction patterns of several natural kaolinite (stacking of different layers) and pyrophyllite (different translation vectors) samples. The models were also successfully tested for the quantification of kaolinite and pyrophyllite in several mineral mixtures. Even mixtures containing both

disordered minerals with additional ordered minerals could be successfully quantified.

The case study at Lagunas Norte demonstrates that quantitative XRD by the Rietveld method can be used as a tool for gold exploration even for rocks that contain minerals with stacking disorder.

[1] Drits, V.A. and Tchoubar, C. (1990) X-ray Diffraction by Disordered Lamellar Structures. Springer-Verlag, Berlin, Heidelberg.
[2] Kogure, T., Jige, M., Kameda, J., Yamagishi, A., Miyawaki, R., and Kitagawa, R., *American Mineralogist*. 2006, 91, 1293-1299.
[3] Treacy, M.M., Newsam, J.M., and Deem, M.W. *Proceedings of the Royal Society of London*. 1991, A433, 499-520.
Bergmann, J., Friedel, P., and Kleeberg, R., *CPD Newsletter*. 1998, 20, 5-8.

Keywords: Rietveld method, stacking disorder, mineral exploration, BGMN

MS01_P19

Nucleation Kinetics of Ligand-Stabilized ZnO Nanoparticles

[A. Windmüller](#)^a, [M. Zobel](#)^a & [R. B. Neder](#)^a

^aUniversity of Erlangen, Germany, e-mail: anna.windmueller@fau.de

Semiconductor nanoparticles such as zinc oxide (ZnO) are commonly produced in sol-gel processes. In order to produce finite-sized nanoparticle, organic ligands are often added as surface stabilizers. The final nanoparticle powders are well characterized with respect to their particle size, crystallinity and stability. Synthesis parameters are optimized regarding particle properties and yield. Nevertheless, it is not yet understood how the different synthesis parameters influence the nucleation kinetics [1].

Time-resolved pair distribution function (PDF) studies have become possible thanks to the advent of the Rapid Acquisition PDF method. In aqueous solutions, smallest molecular clusters of zirconia-sulfate oligomers became accessible [2] and the precursor formation and growth of CeO₂ nanoparticles in hydrothermal synthesis could be followed [3].

These experiments are, to our knowledge, the first in-situ PDF studies in organic solvents with a 30 second time resolution at concentrations below 30 mM. We inject the organic base tetramethylammoniumhydroxide (TMAH) by external software control with a syringe pump into 150 mL of a 30 mM zinc acetate solution in ethanol with the organic ligand 1,5-diphenyl-1,3,5-pentanetrione, which stabilizes the final nanoparticle to a size of < 2 nm. In order to study the dependence of the reaction kinetics on the reaction time and TMAH

amount, we added the TMAH at different speeds of 0.05, 0.15 and 0.25 mL/min as well as with rapid injection to an overall ratio of $[\text{OH}^-]/[\text{Zn}^{2+}] = 2.5$ (equal 4.5 mL) and observed the evolution of the nanoparticle size and crystallinity over time.

Our in-situ PDF studies reveal that the speed of TMAH addition influences the threshold concentration of TMAH above which ZnO nanoparticles start to form as well as how fast the reaction proceeds. The nucleation kinetics appear to be not solely dependent on the concentration of the reactants, but also strongly on the reaction time.

-
- [1] Ludi, B. & Niederberger, M., Dalton Trans. 2003, 42, 12554
[2] Y.-J. Hu, K. E. Knope, S. Skanthakumar, et al., J. Am. Chem. Soc. 2013, 135 (38), 14240
[3] Tyrsted, Ch., Jensen, K. M. O., Bojesen, E. D., et al., Angew. Chem. 2012, 124, 9164

Keywords: nanoparticle, nucleation, in-situ PDF

*Microsymposium MS02:
Ab initio Structure Solutions*

*Chairs: Anton Meden, University of Ljubljana (SI)
Vincent Favre-Nicolin, CEA (Grenoble, F)*

*Microsymposium: Tuesday 17 June 2014 Afternoon – Chemistry AUD I, 1514-213
Poster session: Tuesday 17 June 2014 – iNANO building, 1590-Foyer*

MS02_K1

Structure solution of molecular compounds using direct-space local LS minimizations and cluster-based direct methods.

[Oriol Vallcorba^a](#) & [Jordi Rius^b](#)

^a ALBA-CELLS Synchrotron Light Source,
Crta BP 1413 Km 3.3, 08290 Cerdanyola del Vallès, Barcelona, Spain

^b Institut de Ciència de Materials de Barcelona (CSIC) Campus de la UAB
,08193 Bellaterra, Barcelona, Spain

Choosing the most convenient strategy for solving crystal structures from powders [1] strongly depends on the composition of the sample, the type of compound and the quality (accuracy, completeness, resolution range and peak overlap) of the diffraction data.

For molecular compounds, especially if they do not contain strong scattering atoms, direct methods (DM) can hardly be applied and the use of global optimization (GO) methods working in direct space is the most viable alternative. Within the wide range of GO strategies [2] we have developed TALP [3], which is based on local least-squares minimizations and has proved to be very effective in solving molecular crystal structures. It has been recently applied to diffraction data of limited quality to solve complex crystal structures with more than one independent molecule in the unit cell.

On the other hand, it has been shown that the recently introduced Cluster-based Patterson-function DM [4] can be successfully applied to powder diffraction data of organic compounds when the experimental resolution is high enough. For powders with good crystallinity, use of synchrotron radiation reduces the peak overlap problem and increases the accessible 2θ range. To improve the quality of the measured intensities, various aspects of the collection strategy have been studied on data measured at the MSPD beamline (ALBA synchrotron) with the time-resolved Mythen-II detector.

[1] (a) Černý R.; Favre-Nicolin V., *Z. Kristallogr.*, 2007, 222, 105-113. (b) David W.I.F.; Shankland, K., *Acta Crystallogr. A*, 2008, 64, 52-64.

[2] Shankland, K.; Spillman, M.; Kabova, E.; Edeley D.; Shankland, N. *Acta Crystallogr. C*, 2013, 69, 1251-1259.

[3] Vallcorba, O.; Rius, J.; Frontera, C.; Miravittles, C. *J. Appl. Crystallogr.* 2012, 45, 1270-1277.

[4] Rius, J. *Acta Crystallogr. A*, 2011, 67, 63-67.

Keywords: cluster-based direct methods, direct-space methods, synchrotron radiation, powder diffraction

MS02_K2

Difficult structures come in a variety of flavors

[Stef Smeets](#), [Catherine Dejoie](#), [Lynne B. McCusker](#) & [Christian Baerlocher](#)

ETH Zurich, Switzerland,
e-mail: stef.smeets@gmail.com

Solving the structure of a polycrystalline material is often fraught with difficulties that are inherent to the material. The data may be of unavoidably poor quality, the sample may contain multiple phases, the reflection overlap may be high, or the structure may simply be complex. The approach to solving a structure will depend upon the problem.

The metal-organic-framework HKUST-1, for example, degrades in the presence of water vapor, but can be reconstructed via a solvent-assisted treatment [1]. To understand this process, synchrotron powder diffraction (SXPDP) data were collected on samples degraded in different ways. The patterns were necessarily of poor quality, and all samples contained multiple phases. In one case, however, only two phases were present and these could be distinguished by their peak shapes. Each was indexed and the structure solved by combining SUPERFLIP [2], simulated annealing, and chemical interpretation. This information then allowed some of the other patterns to be unraveled.

For the zeolite SSZ-87, structure solution from SXPDP data failed, presumably because of the 93% reflection overlap. Fortunately, rotation electron diffraction data [3] were available. Although those data were poor and only 15% complete, they proved to be sufficient for the zeolite-specific program FOCUS [5] to find a model that could then be verified with the SXPDP data.

By taking advantage of the flexible simulated-annealing algorithm in TOPAS [6], the complicated organic cation in SSZ-87 could be located and refined. This approach to the location of species within the pores of a zeolite, a long-standing challenge, has now been applied successfully in several cases.

In the future, XFEL sources will provide new opportunities for solving particularly difficult structures. We are developing a new strategy for the collection and processing of such data, based on the broad-bandpass mode (4% energy bandwidth) that will be provided at SwissFEL [6].

[1] G. Majano, O. Martin, M. Hammes, S. Smeets, C. Baerlocher & J. Pérez-Ramírez, *Adv. Funct. Mater.*, 2014, DOI:10.1002/adfm.201303678 [2] L. Palatinus, G. Chapuis, *J. Appl. Crystallogr.*, 2007, 40, 786-790 [3] D. Zhang, P. Oleynikov, S. Hovmöller & X. Zou, *Z. Kristallogr.*, 2010, 225, 94-102 [4] S. Smeets, L. B. McCusker, C. Baerlocher, E. Mugnaioli & U. Kolb, *J. Appl. Crystallogr.*, 2013, 46, 1017-1023 [5] A. A. Coelho, TOPAS-

Keywords: zeolites, metal-organic frameworks, structure determination, XFEL

Oral Presentations:

MS02_O1

Structural characterization of highly defective metal nitropyrazolates by a combination of Rietveld and Debye Function Analyses.

Federica Bertolotti^a, Angelo Maspero^a, Antonio Cervellino^b, Antonietta Guagliardi^c & Norberto Masciocchi^a

^aUniversità dell'Insubria and To.Sca.Lab, Italy

^bPaul Scherrer Institut, Switzerland

^cIstituto di Cristallografia, CNR, and To.Sca.Lab, Italy

Email: federica.bertolotti@uninsubria.it

Structural disorder can play a crucial role in tuning relevant physical properties of materials, especially when dealing with coordination compounds, whose inherently flexibility offers a large variety of possible structural conformations, molecular geometries and network topologies. [1]

A **multiscale** approach [2], combining structural and microstructural characterization and imaging techniques, was applied in order to tackle an uncommon and so far unsolved structural problem occurring in Group 11 4-NO₂-pyrazolates (npz) and appearing as a rapid (and anisotropic) increase of the XRD peak widths with the scattering angle.

The *average* structure of the [Ag(npz)]₃ and [Cu(npz)]₃ species was determined through *ab-initio* X-ray powder diffraction techniques, [3] and used to infer molecular models of randomly distributed defects within molecular stacks of cyclic, trimeric molecules of idealized D_{3h} symmetry.

In order to recover the structural defectiveness from the experimentally observed diffraction patterns, we proposed different faulted models, characterized by lateral displacement of the [M(npz)]₃ trimers (M = Ag, Cu) within molecular chains with a defined periodicity. Then, we simulated the XRPD traces of ordered and faulted models using a tailored Debye Function Approach (Debussy Suite- release 2.0 [4]) on a number of nanosized molecular clusters of variable size and shape.[5]

Scanning Electron Microscopy characterization shows nanofilaments built by separate blocks, irregularly stacked along their growth direction; in addition, many of these polyfragmented rods have a relevant curvature, as a probable consequence of the presence of crystalline domains progressively shifted one away from each other, and which we interpret as a **mesoscopic** evidence

of our **atomic-scale** models of disorder. Finally, the effects of stacking faults on the electrical properties of **bulk** pellets of $[\text{Ag}(\text{npz})]_3$ have been experimentally and critically evaluated.

Financial support by Cariplo Foundation is acknowledged (Project No. 2011-0289).

[1] Cairns A. B., Goodwin, A. L. *Chem. Soc. Rev.* 2013, 42, 4881-4893. [2] Bertolotti F., Maspero A., Cervellino A., Guagliardi A. and Masciocchi N., 2014. *Submitted*. [3] TOPAS-R, V.4.0; Bruker AXS: Karlsruhe, Germany, 2006. [4] Cervellino A., Frison R., Bertolotti F., Guagliardi A., 2014, *in preparation*. [5] Cernuto, G., Masciocchi, N., Cervellino, A., Colonna G. M., Guagliardi. A. *J. Am. Chem. Soc.* 2011, 133, 3114- 3119.

Keywords: Pyrazolates, Ab-initio structure solution, Total Scattering, Stacking Faults.

MS02_O2

SDPD of nanocrystalline organic compounds without prior indexing using a fit by similarity measure based on cross-correlation functions

[Martin U. Schmidt](#), [Stephan Habermehl](#) & [Sonja M. Hammer](#)

Goethe University, Frankfurt am Main, Germany, e-mail: m.schmidt@chemie.uni-frankfurt.de

Rietveld refinements generally fail, if the lattice parameters of the structural model differ more than slightly from the correct lattice parameters and the simulated reflections do not overlap with the experimental ones. For molecular crystals, we developed a more robust fitting algorithm, which uses the cross-correlation function between calculated and experimental powder diagrams, and allows a fit with deviating lattice parameters (FIDEL). The method also works for nanocrystalline organic compounds showing only 10-20 peaks in their powder diagram.

The FIDEL method has been proven to be useful for various applications, including refinements starting from (1) crystal data of an isostructural chemical derivative; (2) crystal data of an isostructural hydrate or solvate; (3) crystal data measured at another temperature (e.g. for fitting a room-temperature powder diagram starting from single-crystal data measured at 100 K).

FIDEL is also used for determining crystal structures from non-indexed powder diagrams of nanocrystalline organic compounds. Three steps are performed: (1) Prediction of possible crystal structures in various space groups using global lattice-energy minimizations by force-field methods. (2) FIDEL fit of 100 to 600 low-

energy structures to the experimental powder diagram. The correct structure results in a good fit, whereas all other structures do not. (3) Rietveld refinement.

The FIDEL method was used to determine the hitherto unknown crystal structure of the nanocrystalline triclinic α -phase of 2,9-dichloroquinacridone ($\text{C}_{20}\text{H}_{10}\text{Cl}_2\text{N}_2\text{O}_2$) from a powder diagram showing 12 broad lines only.

[1] S. Habermehl, P. Mörschel, P. Eisenbrandt, S.M. Hammer, M.U. Schmidt, *submitted*.

Keywords: Structure determination from powder data, molecular compounds, nanocrystalline compounds, FIDEL fit, quinacridone

MS02_O3

The crystal structure of the new $\text{Rb}_2\text{MnP}_2\text{O}_7 \cdot \text{H}_2\text{O}$ diphosphate - *ab initio* determination from X-ray powder diffraction data.

[Stanislav Péchev](#)^a, [Saida Kaoua](#)^b, [Saida Krimi](#)^b, [Pierre Gravereau](#)^a, [Jean-Pierre Chaminade](#)^a & [Abdelaziz El Jazouli](#)^c

^aCNRS, Université de Bordeaux, ICMCB, 87 avenue du Dr. A. Schweitzer, Pessac, F-33608, France.

^bLaboratoire de Physico Chimie des Matériaux Inorganiques, Faculté des Sciences Ain Chock, Casablanca, Morocco.

^cLaboratoire de Chimie des Matériaux Solides, Faculté des Sciences Ben M'Sik-UH2M, Casablanca, Morocco.
e-mail: pechev@icmcb-bordeaux.cnrs.fr

The crystal structure of the new $\text{Rb}_2\text{MnP}_2\text{O}_7 \cdot \text{H}_2\text{O}$ diphosphate was determined from in-house powder diffraction data. An initial *ab initio* structure solution was obtained using direct-space methods based on a Monte-Carlo global optimization process and parallel tempering algorithm with FOX program [1]. The final crystal structure was refined with the Rietveld method using the FullProf Suite programs [2]. Difference Fourier maps were used during the refinement process to adjust the oxygen atomic positions. The microstructural effects of the sample were also treated in the profile refinement.

$\text{Rb}_2\text{MnP}_2\text{O}_7 \cdot \text{H}_2\text{O}$ crystallizes in the monoclinic $P2_1/c$ space group with lattice parameters $a = 5.3836(1)\text{Å}$, $b = 10.2428(1)\text{Å}$, $c = 15.5411(2)\text{Å}$, $\beta = 93.11(2)^\circ$, $Z = 4$, $V = 855.11(2)\text{Å}^3$.

The structure can be described as a single axe stacking of undulating $[\text{MnP}_2\text{O}_{10}]_\infty$ layers; Rb occupy the interlayer spaces. The water molecule is positioned also between the layers. Its presence is confirmed by the

1607cm⁻¹, 3173cm⁻¹ and 3545cm⁻¹ absorption bands observed in the infrared spectrum.

Rb₂MnP₂O₇·H₂O is one of the last members of the A₂MnP₂O₇ (A = Li, Na, K, Rb, Cs) family where every phosphate adopts a different crystal structure with either layered or 3D [MnP₂O₇] frameworks and various Mn coordination [3 - 6]. Although structural filiations being difficult, some parallel can be made between the structures of the Rb and Cs-based compounds and some phosphates of the enlarged A₂MP₂O₇ family like K₂CuP₂O₇ [7].

[1] V. Favre-Nicolin and R. Černý, *J. Appl. Cryst.* (2002) 35, 734. [2] J. Rodríguez-Carvajal, *CPD (IUCr) Newsletter* (2001) 26, 12. [3] S. Kaoua, S. Krimi, S. Péchev, P. Gravereau, J-P. Chaminade, M. Couzi, A. El Jazouli, *J. Solid State Chem.* (2013) 198, 379. [4] L. Adam, A. Guesdon, B. Raveau, *J. Solid State Chem.* (2008) 181, 3110. [5] A. El Maadi, A. Boukhari, E.M. Holt and S. Flandrois, *C.R.Acad. Sci. Paris, Set. II*, (1994) 318, 765. [6] N.K.Lokanath, M.A. Sridhar, J. Shashidara Prasad, G.S. Gopalakrishnan, K.G. Ashamanjari, *Bulletin of Materials Science (Bangalore)* (2000), 23(3), 175. [7] A. ElMaadi, A. Boukhari, and E.M. Holt, *J. Alloys and Compounds* 223 (1995) 13.

Keywords: Diphosphate, structure, layered

MS02_O4

Accurate bond lengths from XRPD via meta-refinement

Ivan S. Bushmarinov & Artem O. Dmitrienko

^aInstitute of Organoelement Compounds RAS,
119991 Vavilova St. 28, Moscow, Russia,
e-mail: ib@ineos.ac.ru

The average precision of bond lengths obtained from Rietveld refinement is usually quoted as 0.03-0.05 Å. However, there is no way to estimate this error without single-crystal data, and unrestrained refinement usually results in larger bond distortions. Actually, the combination of low-quality powder pattern and restrained refinement, typical for laboratory datasets, often makes difficult to check if the refined structure is valid at all [1]. Recently we have developed an automated approach to structure verification based on a new restraint model and statistical analysis of bond deviations from the restrained values [2] and applied it to Rietveld refinement of organic and coordination compounds [3-5].

However, the practice has shown that our approach only allowed to identify local “wrong” bonds in the model and did not provide a general assessment of the model and data quality: both low- and high-quality datasets provided similar verification results, while it was obvious that high-quality data was more sensitive to small errors in the restraint values.

In this report, we introduce a meta-refinement procedure for estimation of the “validity ranges” for bond lengths in the model, which works as a direct measure of refinement accuracy, independent from R-values or crystallographer’s biases. The improved statistical analysis employed even allows the use of conventional “parabolic” restraints, making the method accessible to the users of all Rietveld refinement codes. A small round robin was held to demonstrate the applicability of the approach to datasets measured in different experimental conditions. Since the meta-refinement allows reaching and verifying bond length uncertainties as small as 0.015 Å, it can compete as a source of accurate structures with periodic structure calculations, which have their own biases. The cases of a clathrochelate complex and a substituted nitrofurazan, where the quantum-chemical approach failed for different reasons, are discussed in detail.

[1] J. Brüning, E. Alig, J. van de Streek, M. U. Schmidt, *Z. Für Krist.* 2011, 226, 476. [2] I. S. Bushmarinov, A. O. Dmitrienko, A. A. Korlyukov, M. Y. Antipin, *J. Appl. Crystallogr.* 2012, 45, 1187. [3] S. Shuvaev, I. S. Bushmarinov, I. Sinev, A. O. Dmitrienko, K. A. Lyssenko, V. Baulin, W. Grünert, A. Y. Tsivadze, N. Kuzmina, *Eur. J. Inorg. Chem.* 2013, 2013, 4823. [4] V. V. Popov, S. A. Amelichev, I. S. Bushmarinov, L. S. Konstantinova, K. A. Lyssenko, L. V. Mikhailchenko, V. V. Novikov, V. P. Gulytai, O. A. Rakinin, *Tetrahedron* 2013, 69, 8790. [5] M. I. Pleshchev, V. V. Kachala, A. S. Goloveshkin, I. S. Bushmarinov, V. V. Kuznetsov, D. V. Khakimov, N. N. Makhova, *Mendeleev Commun.* 2013, 23, 271.

Keywords: structure solution, Rietveld refinement, restraints, verification

Posters:

MS02_P20

X-ray powder diffraction as a tool to structural determination of bioactive N-acylhydrazone compounds

Fanny N. Costa^a, Tiago F. da Silva^b, Lidia M. Lima^b, Eliezer J. Barreiro^b, Delson Braz^b, Marcos V. Colaço^c, Letícia Kuplich^c, Regina C. Barroso^c & Fabio F. Ferreira^a

^aUniversidade Federal do ABC, Brazil, e-mail: fanny.costa@ufabc.edu.br;

^bUniversidade Federal do Rio de Janeiro, Brazil;

^cUniversidade do Estado do Rio de Janeiro, Brazil.

The bioactive *N*-acylhydrazone (NAH) moiety has been identified in a great number of lead compounds that act on different types of molecular targets [1]. The compound (*E*)-*N*'-benzylidenecyclohexanecarbohydrazide, herein referred to as LASSBio-1601, was initially obtained as part of a project of synthesis of novel anti-inflammatory and analgesic leads with a *N*-acylhydrazone scaffold. Because of the assemblage of amide and imine functions, NAH compounds may exist as C=N double bond stereoisomers (*E/Z*) and as *syn/antiperiplanar* conformers about the amide CO-NH bond [2].

The complete knowledge of structure, including stereochemistry, is essential for lead optimization in drug discovery [3].

In this work we describe our studies concerning the elucidation of the crystal structure of LASSBio-1601 using X-ray powder diffraction data [4]. This compound crystallizes in the triclinic space group P-1 with unit cell dimensions $a = 4.7912(3) \text{ \AA}$, $b = 10.8640(6) \text{ \AA}$, $c = 15.8300(8) \text{ \AA}$, $\alpha = 52.2773(9)^\circ$, $\beta = 99.333(1)^\circ$, $\gamma = 99.609(1)^\circ$, $V = 640.70(6) \text{ \AA}^3$. The crystal structure of LASSBio-1601 is comprised by two formula units per unit cell ($Z = 2$), accommodating one molecule in the asymmetric unit ($Z' = 1$).

The goodness-of-fit indicator and *R*-factors were, respectively: $\chi^2 = 0.832$, $R_{\text{Bragg}} = 0.666\%$, $R_{\text{wp}} = 2.005\%$ and $R_{\text{exp}} = 2.408\%$. Moreover, nuclear magnetic resonance (NMR) spectroscopy, high-performance liquid chromatography (HPLC) experiment, mass spectroscopy and *in silico* studies were also performed in order to increase information about structural characteristics of this molecule both in the solid state as well as in solution.

[1] Duarte, C.D.; Barreiro, E.J.; Fraga, C.A.M., *Mini Rev. Med. Chem.* 2007, 7, 1108-1119. [2] Palla, G.; Predieri, G.; Domiano, P., *Tetrahedron*, 1986, 42, 3649-3654. [3] Lopes, A.B., Miguez, E., Kümmerle, A.E., Rumjanek, V.M., Fraga, C.A.M., *Molecules*, 2013,

18, 11683-11704. [4] Ferreira, F.F., Antonio, S.G., Rosa, P.C.P., Paiva-Santos, C.O., *Journal of Pharmaceutical Sciences*, 2010, 99, 1734-1744.

Keywords: Crystal structure determination, *N*-acylhydrazone, X-ray powder diffraction.

MS02_P21

Structural characterization of albendazole with the use of x-ray powder diffraction

Kelly Lixandrão^a & Fabio Ferreira^a

^aUFABC, Brazil, kelly.silva@ufabc.edu.br.

Polycrystalline drugs may present polymorphism (property of a substance to crystallize in more than one form or crystal structure). These variations can cause changes in the physical-chemical properties and differences between the polymorphs such as shape, solubility, density, melting range, among other consequences, can lead to formulations that are not effective or even undesired, although the chemical formula is the same [1]. Drugs such as albendazole (chemical formula $\text{C}_{12}\text{H}_{15}\text{N}_3\text{O}_2\text{S}$), which is one of the most effective anthelmintics, [2] showing activity against nematodes, trematodes and cestodes, reasons that added to its safety and low cost have made it a drug widely used in human and veterinary medicines [3]. The X-ray powder diffraction is a powerful technique used in the structural characterization of drugs, and coupled with the Rietveld method [4], the quantification of the active pharmaceutical ingredient (APIs) phases, through the knowledge of their crystal structures, becomes possible. In this paper we discuss some results on the differences between the polymorphs of albendazole, with data obtained by means of X-ray diffraction, thermal analysis (differential scanning calorimetry and thermogravimetric analysis), Fourier transform infrared spectroscopy and scanning electron microscopy.

[1] Maria J., *Polimorfismo de fármacos*. Universidade de São Paulo, São Paulo, 2009. [2] Pranzo M.B., et. al, *Enantiotropically Related Albendazole Polymorphs*. *Journal of Pharmaceutical Sciences*. 2010, Vol. 99, 3731-3742. [3] Campbell, W.C., *The chemotherapy of parasitic infections*. *J Parasitol* 1986, 72: 45-61. [4] Rietveld H. M., *J. Appl. Crystallogr* 1969, 2, 65.

Keywords: albendazole, crystal structure, polymorphism, X-ray powder diffraction, Rietveld method.

Crystal Structure Determination of (±)-Mefloquine Hydrochloride Using X-Ray Powder Diffraction Data.

Vania Mendes do Prado^a & Fabio Furlan Ferreira^a

^aUniversidade Federal do ABC, Brazil, vania_mp@yahoo.com.br

(±)-Mefloquine hydrochloride (MEFHCl), is an effective antimalarial agent and presents the polymorphism phenomenon. Many authors have studied the tetragonal structure of MEFHCl, but there are still doubts regarding the nature of the tetragonal species. Karle and Karle (1991)[1] reported a tetragonal structure ($P4_2/n$, origin at center of symmetry) for MEFHCl·1/2(methanol) solvate, and some reservations regarding whether the solvate incorporated was methanol or water have been made. Pitaluga *et al.* (2010)[2] studied the tetragonal species using single-crystal synchrotron data collected at 120 K, however, the same doubts about the nature of the species was found. In this work, the tetragonal structure of mefloquine hydrochloride was studied in details by X-ray powder diffraction (XRPD) and Fourier transform infrared spectroscopy (FTIR). By means of a structural determination, using the DASH software package, was found the following values: $a = 24.5639 \text{ \AA}$, $b = 24.5639 \text{ \AA}$, $c = 6.38686 \text{ \AA}$, $\alpha = 90^\circ$, $\beta = 90^\circ$, $\gamma = 90^\circ$, $V = 3853.74 \text{ \AA}^3$, the highest figure-of-merit $M(25) = 34.9$, $F(25) = 79.7$ and space group $P4_2/n$. The best solution found clearly indicates the presence of voids in the unit cell. Thus, we found the same doubts presented already about the nature of the tetragonal species, is a hydrate or a solvate. To try to resolve this issue, we considered the presence of water within the unit cell, filling up the voids and refining the structure through the Rietveld method. Finally it was found that the resolved crystal structure for tetragonal hydrated mefloquine hydrochloride consists of four formula units per unit cell ($Z = 4$) of a racemic mixture of erythro isomers, thus accommodating 8 mefloquine hydrochloride and 4 water molecules within the unit cell. FTIR data have supported this assertion.

[1] J. M. Karle and I. L. Karle, *Acta Crystallogr. C*, 1991, 47, 2391–2395. [2] A. Pitaluga, L. D. Prado, R. Seiceira, J. L. Wardell, and S. M. S. V Wardell, *Int. J. Pharm.*, 2010, 398, 50–60.

Keywords: Mefloquine hydrochloride, tetragonal structure and X-ray powder diffraction.

Determination of Pure Organic Charge-Transfer molecules from PXRD data: The crystal structure of the carbazole-TTM radical

Carles Miravittles^a, Jordi Rius^a, Lluís Julià^b, Lluís Fajari^b & Oriol Vallcorba^a

^a Institut de Ciència de Materials de Barcelona (CSIC) Campus de la UAB, 08193 Bellaterra, Catalunya, Spain

^b Departament de Química Biològica i Modelització Molecular, Institut de Química Avançada de Catalunya (CSIC) Jordi Girona 18-26 08034 Barcelona Spain

In the course of the research on pure organic charge-transfer molecules based on the tris(2,4,6-trichlorophenyl)-methyl radical (TTM), it was necessary to solve the crystal structure of the [4-(*N*-carbazolyl)-2,6-dichlorophenyl]bis(2,4,6-trichlorophenyl)methyl radical. After multiple unsuccessful attempts of growing single-crystals, powder diffraction data of the radical adduct were measured in the laboratory. Since the data could not be indexed, a transmission synchrotron powder pattern was collected at ID31 Beamline (ESRF) at 100 K ($\lambda = 0.62085 \text{ \AA}$). In this second attempt the indexing was successful, the difficulty being the presence of a small impurity: $a = 11.818$, $b = 11.822$, $c = 12.716 \text{ \AA}$, $\alpha = 104.21$, $\beta = 114.67$, $\gamma = 106.66^\circ$, $V = 1404 \text{ \AA}^3$, space group $P-1$, $C_{31}H_{14}Cl_{18}N$, $Z = 2$.

The intensities extracted from pattern matching with DAJUST [1] were introduced in the direct-space structure solution program TALP [2] which supplied the correct model. The final atomic coordinates were refined with the restrained Rietveld program RIBOLS [3]. The crystal structure packing of the radical adduct is characterized by the formation of two dimeric units propagating along the normal to the a^* plane [4].

[1] Vallcorba, O.; Rius, J.; Frontera, C.; Peral, I.; Miravittles, C. *J. Appl. Crystallogr.* 2012, 45, 844-848.

[2] Vallcorba, O.; Rius, J.; Frontera, C.; Miravittles, C. *J. Appl. Crystallogr.* 2012, 45, 1270-1277.

[3] Rius, J. RIBOLS18: A computer program for least-squares refinement from powder diffraction data.

[4] Fajari, L.; Papoular, R.; Reig, M.; Brillas, E.; Jorda, J.; Vallcorba, O.; Rius, J.; Velasco, D.; Julià, L. *J. Org. Chem.* 2014, 79, 1771-1777.

Keywords: carbazole, direct-space methods, synchrotron radiation

The crystal structure of the new $\text{Rb}_2\text{MnP}_2\text{O}_7 \cdot \text{H}_2\text{O}$ diphosphate - *ab initio* determination from X-ray powder diffraction data.

Stanislav Péchev^a, Saida Kaoua^b, Saida Krimi^b, Pierre Gravereau^a, Jean-Pierre Chaminade^a & Abdelaziz El Jazouli^c

^aCNRS, Université de Bordeaux, ICMCB, 87 avenue du Dr. A. Schweitzer, Pessac, F-33608, France.

^bLaboratoire de Physico Chimie des Matériaux Inorganiques, Faculté des Sciences Ain Chock, Casablanca, Morocco.

^cLaboratoire de Chimie des Matériaux Solides, Faculté des Sciences Ben M'Sik-UH2M, Casablanca, Morocco.
e-mail: pechev@icmcb-bordeaux.cnrs.fr

The crystal structure of the new $\text{Rb}_2\text{MnP}_2\text{O}_7 \cdot \text{H}_2\text{O}$ diphosphate was determined from in-house powder diffraction data. An initial *ab initio* structure solution was obtained using direct-space methods based on a Monte-Carlo global optimization process and parallel tempering algorithm with FOX program [1]. The final crystal structure was refined with the Rietveld method using the FullProf Suite programs [2]. Difference Fourier maps were used during the refinement process to adjust the oxygen atomic positions. The microstructural effects of the sample were also treated in the profile refinement. $\text{Rb}_2\text{MnP}_2\text{O}_7 \cdot \text{H}_2\text{O}$ crystallizes in the monoclinic $P2_1/c$ space group with lattice parameters $a = 5.3836(1)\text{Å}$, $b = 10.2428(1)\text{Å}$, $c = 15.5411(2)\text{Å}$, $\beta = 93.11(2)^\circ$, $Z = 4$, $V = 855.11(2)\text{Å}^3$. The structure can be described as a single axis stacking of undulating $[\text{MnP}_2\text{O}_{10}]_\infty$ layers; Rb occupy the interlayer spaces. The water molecule is positioned also between the layers. Its presence is confirmed by the 1607cm^{-1} , 3173cm^{-1} and 3545cm^{-1} absorption bands observed in the infrared spectrum. $\text{Rb}_2\text{MnP}_2\text{O}_7 \cdot \text{H}_2\text{O}$ is one of the last members of the $\text{A}_2\text{MnP}_2\text{O}_7$ ($A = \text{Li}, \text{Na}, \text{K}, \text{Rb}, \text{Cs}$) family where every phosphate adopts a different crystal structure with either layered or 3D $[\text{MnP}_2\text{O}_7]$ frameworks and various Mn coordination [3 - 6]. Although structural filiations being difficult, some parallel can be made between the structures of the Rb and Cs-based compounds and some phosphates of the enlarged $\text{A}_2\text{MP}_2\text{O}_7$ family like $\text{K}_2\text{CuP}_2\text{O}_7$ [7].

[1] V. Favre-Nicolin and R. Černý, *J. Appl. Cryst.* (2002) 35, 734. [2] J. Rodríguez-Carvajal, *CPD (IUCr) Newsletter* (2001) 26, 12. [3] S. Kaoua, S. Krimi, S. Péchev, P. Gravereau, J.-P. Chaminade, M. Couzi, A. El Jazouli, *J. Solid State Chem.* (2013) 198, 379. [4] L. Adam, A. Guesdon, B. Raveau, *J. Solid State Chem.* (2008) 181, 3110. [5] A. El Maadi, A. Boukhari, E.M. Holt and S. Flandrois, *C.R.Acad. Sci. Paris, Set. II*, (1994) 318, 765. [6] N.K.Lokanath, M.A. Sridhar, J. Shashidara Prasad, G.S. Gopalakrishnan, K.G. Ashamanjari, *Bulletin of Materials Science (Bangalore)* (2000), 23(3), 175. [7] A. ElMaadi, A. Boukhari, and E.M. Holt, *J. Alloys and Compounds* 223 (1995) 13.

Keywords: Diphosphate, structure, layered

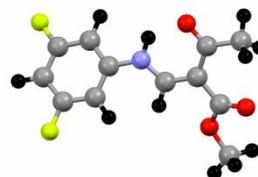
(Z)-methyl 2-((3, 5- difluoro phenyl-amino) methylene) - 3 -oxobutanoate - powder diffraction and solid state DFT study

Ľ.Smrčok^a & V.Milata^b

^aInstitute of Inorganic Chemistry, Slovak Academy of Sciences, SK-845 36 Bratislava, Slovak Republic, e-mail: uachsmrk@savba.sk,

^bInstitute of Organic Chemistry, Catalysis and Petrochemistry, Faculty of Chemical and Food Technology, Slovak University of Technology, SK-812 37 Bratislava, Slovak Republic, e-mail : viktor.milata@stuba.sk

Mono- and polyfluorinated arylaminomethylene derivatives are frequently used precursors for synthesis of well-known group of antibacterial agents - fluoroquinolones. Therefore study of its structure is very



important, especially from the point of view geometrical isomerism, intramolecular hydrogen bond between hydrogen atom of iminogroup and oxygen atom of carbonyl group of alkoxy carbonyl vs. acetyl group and fluorine interactions or supramolecular structure. Crystal structure of the title compound was solved from X-ray powder diffraction data and refined by geometry optimization by total energy minimization in the solid state. The structure is monoclinic ($P2_1/c$, $Z=4$) with the non-planar molecules linked, apart for electrostatic interactions, by

weak C-H...O bonds.

Financial support of the Slovak Research and Development Agency under the contract No. APVV-0038-11 and Slovak Grant Agency VEGA (1/0829/14) is acknowledged.

Keywords: crystal structure, DFT, fluoroquinolone

Computational Pharmaceutical Materials Science

Jacco van de Streek^a, Kristoffer Johansson^a & Xiaozhou ms^a

^aUniversity of Copenhagen, Denmark, e-mail: jacco.vandestreek@sund.ku.dk

The five Crystal-Structure Prediction (CSP) Blind Tests have shown that molecular-mechanics force fields are not accurate enough for crystal structure prediction [1].

The first—and only—method to successfully predict all four target crystal structures of one of the CSP Blind Tests was dispersion-corrected Density Functional Theory (DFT-D), and this is what we use for our work.

However, quantum-mechanical methods (such as DFT-D), are too slow to allow simulations that include the effects of time and temperature, certainly for the size of molecules that are common in pharmaceutical industry. Including the effects of time and temperature therefore still requires molecular dynamics (MD) with less accurate force fields.

In order to combine the accuracy of the successful DFT-D method with the speed of a force field to enable molecular dynamics, our group uses Tailor-Made Force Fields (TMFFs) as described by Neumann [2]. In Neumann's TMFF approach, the force field for each chemical compound of interest is parameterised from scratch against reference data from DFT-D calculations; in other words, the TMFF is fitted to mimic the DFT-D energy potential. Parameterising a dedicated force field for each individual compound requires an investment of several weeks, but has the advantage that the resulting force field is more accurate than a transferable force field.

Combining Crystal Structure Prediction with DFT-D followed by Molecular Dynamics with the Tailor-made force field allows us to calculate *e.g.* the temperature-dependent unit-cell expansion of each predicted polymorph, as well as possible temperature-dependent disorder. This is relevant for example when comparing the calculated X-ray powder diffraction patterns of the predicted crystal structures against experimental data.

[1] D. A. Bardwell *et al.*, *Acta Cryst.* 2011, B67, 535 [2] M. A. Neumann, *J. Phys. Chem. B* 2008, 112, 9810.

Keywords: Crystal-structure prediction, Density Functional Theory, Molecular Dynamics

*Microsymposium MS03:
Biological and Molecular Materials*

Chairs: Andy Fitch, ESRF (Grenoble, F)

Kenny Ståhl, Technical University of Denmark (DK)

Microsymposium: Monday 16 June 2014 Morning – iNANO building, 1593-012

Poster session: Monday 16 June 2014 – iNANO building, 1590-Foyer

MS03_K1

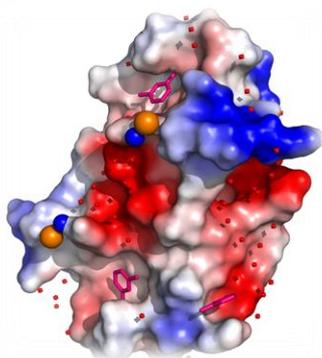
Macromolecular Powder Diffraction: Perspectives in Drug Discovery.

F. Karavassili^a, A. E. Giannopoulou^a, K. Magioul^a, A. Valmas^a, M. Norrman^b, G. Schluckebier^b, J. Wright^c, A. Fitch^c & I. Margiolaki^a

^aDepartment of Biology, Section of Genetics, Cell Biology and Development, University of Patras, GR-26500, Greece.

^bDiabetes Protein Engineering, Novo Nordisk, A/S, Novo Nordisk Park, DK-2760 Malov, Denmark.

^cEuropean Synchrotron Radiation Facility, BP-220, F-38043, Grenoble Cedex 9, France.



The study of biological macromolecules in the absence of good quality single crystals is a challenging field which attracts particular scientific interest in recent years. The development of the X-ray powder diffraction methods and algorithms has already allowed for the structural characterization of a range of proteins and has been established as a useful complementary technique to the traditional single crystal diffraction techniques.^{1,2}

Protein polycrystalline samples often form in a short period of time and under different conditions of physico-chemical environment. To date, our studies on complexes of human insulin with organic ligands,^{3,4} revealed a high degree of polymorphism, as well as crystalline polymorphs which were not previously identified probably due to the lack of adequate tools to characterize microcrystalline protein precipitates. Part of these results and the potential use of the newly identified polymorphs in future drugs to treat epidemics such as diabetes correspond to the main topic of this talk.

[1] Von Dreele, R. B., Methods Enzymol. 2003, **368**, 254-267. [2] Margiolaki, I. & Wright, J. P., Acta Cryst. 2008, **A64**, 169-180. [3] Karavassili, F. et al. Acta Cryst. 2012, **D68**, 1632-1641. [4] Margiolaki, I. et al., Acta Cryst. 2013, **D69**, 978- 990.

Keywords: structural biology, human insulin, macromolecular powder diffraction

MS03_K2

Advances in Synchrotron XRPD for Enhanced Characterization of Pharmaceuticals.

Paolo P. Mazzeo^a & Fabia Gozzo^{a,b}

^a Excelsus Structural Solutions(Swiss)AG

^b Excelsus Structural Solutions sprl

X-ray Powder Diffraction (XRPD) is for sure the most important technique to investigate pharmaceutical samples in their solid state (i.e polymorphs, solvates, hydrates, salts, co-crystals, amorphous). The use of synchrotron radiation further enhanced XRPD capabilities allowing great improvements in the pharmaceuticals characterization.

Pharmaceutical drug substances can exist in different solid-state forms. This *polymorphism* can play a key role on the quality and performances of drugs since it can strongly affect their physic-chemical properties (e.g solubility, bioavailability, efficacy, safety). It is in fact a regulatory requirement to conduct detailed analyses of the solid state properties of both drug substance and product during its technical development and later on during manufacturing and storage.

Synchrotron XRPD dramatically pushes the limits of conventional X-ray sources offering the advantages of ultra-high FWHM and d-spacing resolutions, accurate 2 θ angle assignment, high signal-to-background and signal-to-noise ratios. When coupled with new cutting-edge single-photon-counting detection systems, the measurements times is drastically reduced to milliseconds, allowing *in-situ* dynamic study of the kinetic of transformations and radiation-damage-free high-resolution diffraction patterns.

We discuss advances in instrumentation, calibration and data collection procedures leading to detection limits of contaminating crystalline phases in different formulations better than 0.05% wt% as well as the disclosure of subtle structural details. We describe the technique, the instrumentation and discuss relevant examples of applications focused on pharmaceuticals. The modalities of the fast, easy and affordable access to these state-of-the-art analytical tools are also discussed.

Keywords: Synchrotron, Pharmaceuticals, SR-XRPD

Oral Presentations:

MS03_O1

Using synergy of experimental and computational techniques to solve monomer-trimer dilemma

[Dubravka Šišak Jung](#)^a, [Tomica Hrenar](#)^b, [Petra Kalinovič](#)^b & [Ozren Jović](#)^b

^aDECTRIS Ltd, Switzerland

^bUniversity of Zagreb, Faculty of Science, Department of Chemistry, Croatia
e-mail: dubravka.sisak@dectris.com

2-(methylideneamino)acetonitrile (MAAN) has raised some interest in the 1970ies, due to its reactivity with aminoacids and formation of peptides [1,2]. Reports on its chemical properties also included ability to polymerize. However, physical characterization of monomer and trimer appears to be comparably limited.

In this work, we expand the solid-state characterization, and present how synergy of experimental and computational techniques can lead to a full and reliable analysis of molecular compounds. In the first step, molecular structures of MAAN and its trimer were investigated using computational techniques. In particular, conformational analyses were performed using stochastic search. For conformers that exhibited minimum energy, quantum chemical (density functional theory, DFT) calculations were made. This resulted in optimized molecular structures of both monomer and trimer.

The second step involved characterization of commercial sample. Infrared and Raman spectra were measured, but straightforward monomer-trimer disambiguation was not possible. Therefore, for both monomer and trimer, harmonic and anharmonic vibrational frequencies were calculated using the DFT and coupled cluster theory. Based on the comparison between the experimental and calculated vibrational spectra, it was found that the sample contains MAAN trimer.

This information was used in the third step of this study- structure determination from XPD data. Namely, although the measured pattern was of excellent quality, reciprocal structure determination methods did not work. Therefore, the knowledge of molecular entity and its optimized geometry was crucial. Given that the unit cell volume suggested 8 molecules in the unit cell, and the proposed P21/n symmetry, two trimer molecules were optimized in direct-space, using the program FOX [3]. Restrainted Reitveld refinement of the resulting structure was carried out in XRS suite of programs [4].

As last, computation techniques were used again, to minimize the energy of the crystal cell, and thus serve as a validation tool of the experimentally obtained crystal structure.

[1] A.S. Subbaraman, Z.A. Kazi, A.S.U. Choughuley, and M.S. Chadha, *Origins of Life* 1975, 6, 537–539.

[2] K. Kawashiro, K. Nishiguchi, and T. Nara, *Orig. Life Evol. Biosph.* 1989, 19, 133–142.

[3] Favre-Nicolin, V., Černý, R. *J. Appl. Cryst.* 2002, 35(6), 734–743.

[4] Baerlocher, Ch, Hepp, A. XRS suite, ETH Zurich

Keywords: molecular material, crystal structure, combined methods

MS03_O2

Investigating nanocrystalline drugs embedded in a polymeric matrix by Debye Function Analysis

[Carlotta Giacobbe](#)^a, [Dritan Hasa](#)^b, [Dario Voinovich](#)^b, [Antonio Cervellino](#)^c, [Norberto Masciocchi](#)^a & [Antonietta Guagliardi](#)^d

^aDipartimento di Scienza e Alta Tecnologia, Università dell'Insubria, I-22100 Como, Italy.

carlotta.giacobbe@uninsubria.it

^bDepartment of Pharmaceutical Sciences, University of Trieste, P. le Europa 1, I-34127 Trieste, Italy

^cPaul Scherrer Institut, 5232 Villigen PSI, Switzerland

^dIstituto di Cristallografia, CNR, I-22100 Como, Italy

The release rate of a solid drug is directly related to particle size; smaller crystals have, in fact, an enhanced ability to reach their physiological target^[1]. To this goal, the use of mechanical energy, inducing size/morphological modifications, represents a straightforward, green, and innovative approach. The process takes the name of *mechanochemical activation*, and has recently been introduced as an efficient pharmaceutical processing technique.^[2]

In our work, coground mixtures of Vinpocetine (VIN) (C₂₂H₂₆N₂O₂), a poorly soluble drug used for the treatment of cognitive disorders and related symptoms^[3], and Cross-Linked Polyvinylpyrrolidone (C₆H₉NO)_n (PVP-CL), have been investigated at variable milling time and 1:4 and 1:7 VIN:PVP weight ratios. The Debye Function Analysis (DFA) of several mixtures is applied for the first time to extract information about structure, size and size distribution, morphology and amorphization of drug nanoparticles. To this aim, we used high resolution data collected at the Material Science beamline MS-X04SA of the Swiss Light Source, and the DEBUSSY suite 2.0 of programs^[4] modeling the total (Bragg and diffuse) sample scattering.

Quantitative results on the diverse microstructure modifications controlled by the milling time and the drug-to-polymer ratio will be presented. They show a clear trend between time, size distribution and weight ratio. Moreover, investigations on the biopharmaceutical performance of the most activated systems are in progress to be correlated to the previous results.

Significantly, while other methods are commonly used to characterize nanocrystalline drugs, especially in terms of size and morphology (TEM, HRTEM – at the expenses of sample deterioration), the DFA method here discussed offers a novel, exhaustive (and statistically sound) characterization tool^[5,6].

Support by Fondazione Cariplo (Project No 2009-2446) is acknowledged.

[1] D. Hasa, D. Voinovich, B. Perissutti, A. Bonifacio, M. Grassi, E. Franceschinis, S. Dall'Acqua, M. Speh, J. Plavec, S. Invernizzi. *J. Pharm. Sci.*, 2011, 100, 915. [2] I. Colombo, G. Grassi, M. Grassi. *J. Pharm. Sci.* 2009, 98, 3961. [3] E. Csanda, P. Harcos, Z. Bacsy, R. Berghammer, J. Kenez *Drug Dev. Res.* 1988, 14, 185. [4] A. Cervellino, R. Frison, F. Bertolotti, A. Guagliardi, 2014, *in preparation* [5] J.M. Delgado-Lopez, R. Frison, A. Cervellino, J. Gomez-Morales, A. Guagliardi, N. Masciocchi. *Adv. Funct. Mat.* 2014, 24, 1090. [6] R. Frison, G. Cernuto, A. Cervellino, O. Zaharko, G. M. Colonna, A. Guagliardi, N. Masciocchi. *Chem. Mater.* 2013, 25, 4820.

Keywords: Drug-Polymer Nanocomposites, Size Distribution, Debye Function Analysis

MS03_O3

Fit of organic crystal structures to PDF curves

Dragica Podgorski^a, Martin U. Schmidt^a, Pavol Juhás^b & Simon J. L. Billinge^{b,c}

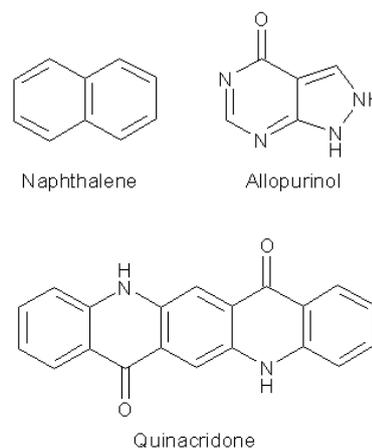
^aGoethe University, Frankfurt am Main, Germany, e-mail: podgorski@chemie.uni-frankfurt.de,

^bBrookhaven National Laboratory, Upton, USA,

^cColumbia University, New York, USA

Local structures in crystalline, nanocrystalline and amorphous organic compounds can be investigated using pair distribution functions (PDF). The experimental determination of the PDF curves of organic compounds is similar to that of inorganic compounds. However, the fit of a structural model to a given PDF curve is at present much more challenging, because the molecular geometry (bond lengths, bond angles, torsion angles) has to be taken into account, and because of differences between inter- and intramolecular vibrational amplitudes. Such fits have rarely been done. [1-3]

We developed a method to perform fits of organic structures to experimental PDF curves using the new Python-driven program package SrFit. [3] Three examples were chosen: crystalline samples of naphthalene and allopurinol, and a nanocrystalline sample of quinacridone.



Synchrotron powder patterns of the three samples were recorded at NSLS (Brookhaven, USA) with $\lambda = 0.18 \text{ \AA}$. From these data the experimental PDF curves were derived with PDFgetX3.

Crystal structural models of the three compounds were fitted to the experimental PDF curves. Bond lengths, bond angles and torsion angles were kept fixed. The molecular position and the spatial orientation of the molecules was fitted together with lattice parameters, scale factor and isotropic displacement parameters. In all cases a good fit to the experimental PDF curves could be achieved. Furthermore, the fit was successful as well, when random values for the molecular position and orientation were chosen as starting points. Hence, the procedure also allows to solve crystal structures of crystalline and nanocrystalline organic compounds by using the PDF curves.

[1] M.T. Dove, M.G. Tucker, D.A. Keen, *Eur. J. Mineral.* 2002, 14, 331-348. [2] N. Rademacher, L.L. Daemen, E.L. Chronister, T. Proffen, *J. Appl. Cryst.* 2012, 45, 482-488. [3] D. Podgorski, P. Juhás, M.U. Schmidt, S.J.L. Billinge, *submitted*. [4] D. Podgorski, P. Juhás, S.J.L. Billinge, M.U. Schmidt, *to be published*.

Keywords: Pair distribution function, PDF, organic compounds, nanocrystalline, quinacridone

Powder Diffraction and DFT Studies of Synthetic Insect Pheromones

Andy Fitch^a, Lee Brooks^{a,b}, Michela Brunelli^c, Philip Pattison^{a,d} & Graeme Jones^b

^aESRF, Grenoble, France, fitch@esrf.fr;

^bKeele University, UK;

^cILL, Grenoble, France;

^dUniversity of Lausanne, Switzerland.

Eight chiral monomethyl alkanes have been synthesized and their crystal structures solved from high resolution powder diffraction patterns collected using synchrotron radiation. Such compounds have been seen to act as recognition pheromones in social insects. Carbon chain lengths varied from C₂₅ to C₃₁ with the methyl group at various positions along the chain. One compound, (S)-7-methylnonacosane, also formed a low quality single crystal from which its structure was solved and refined. Although the powder diffraction patterns were good enough to solve the crystal structures, using the standard technique of real-space simulated annealing, with near-linear molecules, chemically unreasonable distortions occurred during Rietveld refinement unless many distance, angle and torsion restraints were imposed. From the results of the single-crystal structure it is evident that there is a gentle bend in the molecule close to the position of the methyl side chain. Thus imposing a near-linear molecule is incorrect, and giving sufficient freedom in the Rietveld refinement to allow the molecule to bend leads to an inaccurate structure. In short, the correct structure must be known to judge the strength of the restraints to apply, and this must vary at different parts of the chain.

As an alternative to refining the structure from the powder diffraction data, the structures have been optimized via dispersion-corrected DFT calculations [1] starting from the powder structures. Agreement between the single-crystal and DFT-minimized structures is satisfactory, with an rms distance of 0.054 Å and a maximum distance of 0.132 Å when comparing carbon atom positions. With this approach, a well defined structure optimization strategy is used for all the crystal structures. The molecules studied fall into two packing types, (both with monoclinic symmetry), depending on the position of the methyl group on the main carbon chain relative to the overall chain length.

[1] J. van de Streek, M. A. Neumann *Acta Cryst.* 2010, B66, 544.

Keywords: synchrotron radiation, DFT, insect pheromones

The effect of water on the outcome of mechanical treatment in “L-serine-oxalic acid” system

Evgeniy Losev^{a,b} & Elena Boldyreva^{a,b}

^aInstitute of Solid State Chemistry and Mechanochemistry SB RAS, Russian Federation;

^bREC-008, Novosibirsk State University, Russian Federation. E-mail: losev.88@mail.ru

The aim of the present work was to study the effect of water in the “L-serine-oxalic acid” system under mechanical treatment. Both L-serine and oxalic acid can form the hydrates, and it was possible to study the effect of water in various forms on the outcome of mechanochemical reactions.

Co-grinding of dry anhydrous reagents gave only trace amounts of the product phase (anhydrous 1:1 L-serinium oxalate), apparently due to the interaction with the trace amounts of water in the air. Neat co-grinding of anhydrous oxalic acid with L-serine monohydrate or of anhydrous L-serine with oxalic acid dihydrate gave polymorph II (kinetic form).^{1,2} Co-grinding of L-serine monohydrate with oxalic acid dihydrate as well as liquid-assisted grinding with sufficient amount of liquid water added gave polymorph I (thermodynamic form) and polymorph 2 (with a very low transformation degree) if too little water was added.³

Further investigation of the system reveals ability of reaction between L-serine monohydrate and oxalic acid dihydrate without mechanical stress. The storage of the components in sealed vial resulted in formation of I polymorph of [L-serH]₂[Ox]•2H₂O.¹ Moreover an intermediate in the reaction was form II of [L-serH]₂[Ox]•2H₂O.^{1,2}

Based on the obtained results we proposed the outcome of the mechanochemical transformation mostly depends on the total amount of water but not on crystal structure of initial hydrates.

Spray drying and antisolvent crystallisation techniques were also used in order to investigate an influence of conditions on crystallisation process in the system.

The results are analysed on the basis of X-ray powder diffraction, IR-spectroscopy, optical and polarising microscopy data.

The work was supported by the RFBR (Grants No. 12-03-31663 mol-a, 14-03-31866 mol-a, 11-03-00684-a),

by grants from the Russian Ministry of Education and Science No. 14.B37.21.1093, NSH 4357.2010.3, NSH 221.2012.3., programs from RAS 54.38 and 24.38 and Ludo Frevel Crystallography Scholarship Award (2013).

[1] D. Braga, L. Chelazzi, I. Ciabatti and F. Grepioni. *New J. Chem.*, 2013, 37, 97 [2] M. Kulik, A. Pazio and K. Wozniak, *Acta. Cryst.*, 2013, E69, o1667; [3] E.A. Losev, E.V. Boldyreva. *CrystEngComm.*, 2014, DOI: 10.1039/C3CE42321B.

Keywords: mechanochemistry, molecular salt, hydrate, hydrogen bond

MS03_28

Structural and microstructural characterization by X-ray powder diffraction of pharmaceutical co-crystals obtained by precipitation in supercritical CO₂ environment.

[Mathieu Marchivie^a](#), [Clémence Neurohr^b](#) & [Pascale Subra-Paternault^b](#)

^aUniversity of Bordeaux, ICMCB - CNRS UPR 9048, 87 av Dr. Schweizer F-33600 Pessac, France

^bUniversity of Bordeaux, CBMN – CNRS UMR 5248, Allée Geoffroy St Hilaire, F-33600 Pessac, France.

The properties of materials in the solid state are heavily dependent on three-dimensional arrangement adopted by the molecules. Concerning active pharmaceutical ingredients (API), it is well known that properties such as stability, flowability, hygroscopicity or bioavailability, are dependent on the arrangement of molecules in the solid. Thus, different strategies have been proposed to modify and control such properties including the formation of salts, polymorphs, hydrates, solvates and more recently co-crystals. The co-crystals are formed of two (or more) different molecules crystallizing in the same crystal lattice to form a molecular complex.^[1, 2] In the drug design field, such systems are prepared from an API and a second molecule that promotes the formation of the co-crystal, called co-former. While the first co-crystal was discovered in 1844^[2, 3] it is only recently that co-crystals have emerged as promising compounds in drug development to control the solubility, reduce hygroscopicity, control polymorphism and many other features^[1, 4]. Several co-crystal growing techniques have been attempted among which the most commonly used are recrystallization from solvents, from a melt or, in a more innovative way, by precipitation in supercritical CO₂ environment.

X-ray powder diffraction is a powerful tool to identify co-crystals within a mixture, find the proportions and analyse the microstructural features. In this communication, we present the results obtained on several Naproxen – Nicotinamide powder samples that exhibit different microstructural features and different proportions of co-crystal depending on the initial mixture composition and on the different parameters of the process.

[1] N. Qiao, M. Li, W. Schlindwein, N. Malek, A. Davies and G. Trappitt, *Int J Pharm*, 2011, 419, n° 1-2, 1-11
[2] G. P. Stahly, *Crystal Growth & Design*, 2009, 9, n° 10, 4212-4229
[3] F. Wohler, *Annalen Chem. Pharm.*, 1844, 51, 145-163
[4] D. J. Good and N. Rodriguez-Hornedo, *Crystal Growth & Design*, 2009, 9, n° 5, 2252-2264; N. A. Meanwell, *Annual Reports in Medicinal Chemistry*, 2008, 43, 373-404; N. Rodriguez-Hornedo, *Molecular Pharmaceutics*, 2007, 4, n° 3, 299-300; N. Schultheiss and A. Newman, *Cryst Growth Des*, 2009, 9, n° 6, 2950-2967; N. Shan and M. J. Zaworotko, *Drug discovery today*, 2008, 13, n° 9-10, 440-446

Keywords: Pharmaceutical co-crystals, phase identification, microstructure.

MS03_P29

Characterization of hydrochlorothiazide in solid formulations

[Simone Toledo Bonemer de Salvi^a](#), [Antonio Selma Gutierrez^a](#) & [Carlos de Oliveira Paiva Santos^a](#)

^aUniversity of Chemistry, Brazil, e-mail: simonebonemer@yahoo.com.br

Hydrochlorothiazide (HCTZ), C₇H₈ClN₃O₄S₂, is a diuretic and is also used to treat blood pressure (hypertension). This active principle, HCTZ, has two anhydrous polymorphs known, respectively Forms I described by L. Dupont and O. Diderberg [1] and Form II described by A. Florence et al. [2]. In order to characterize solid state, x-ray powder diffraction is a powerful technique and has been successfully applied to investigate polymorphism in medicines. In this work, three tablets of hydrochlorothiazide (a reference and two generics) were analyzed, all samples of 25mg. The data was collected using Rigaku RINT2000 diffractometer cooper rotate anode. The Rietveld method [3] was applied to characterize de polymorphic form of the HCTZ and in the case of crystalline excipients with structure known, this phases could be characterized too. The refinements were performed using TOPAS Academic v.5. software [4]. The results showed that all tablets have the form I of HCTZ and the excipient lactose monohydrate in the crystalline form. One of the generic also exhibited excipient sodium lauryl sulfate in the crystalline form. The results showed

that the Rietveld method is efficient to characterize the crystalline form of the active principle of HCTZ and crystalline excipients lactose monohydrate and sodium lauryl sulfate in solid formulations.

[1] Dupont, L and Dideberg O., *Acta Crystallographica Section B*. 1972, 28, 45 [2] Florence, A. et al, *Acta Crystallographica Section E*. 2005, 61, o2798 [3] Rietveld H.M., *Journal of Applied Crystallography*., 1969, 2, 65. [4] Coelho.A., Software Topas Academic v.5. 2007.

Keywords: Hydrochlorothiazide, polymorphism, x-ray powder diffraction, Rietveld Method.

MS03_P30

Novel crystalline phase and first order phase transitions of human insulin complexed with phenol-derivatives.

A. Valmas^a, F. Karavassili^a, A. E. Giannopoulou^a, Konstantina Magioul^a, M. Norrman^b, G. Schluckebier^b, J. Wright^c, A. Fitch^c & I. Margiolaki^{a,c}

^aDepartment of Biology, Section of Genetics, Cell Biology and Development, University of Patras, GR-26500, Patras, Greece

^bDiabetes Protein Engineering, Novo Nordisk, A/S, Novo Nordisk Park, DK-2760 Malov, Denmark

^cEuropean Synchrotron Radiation Facility, BP-220, F-38043, Grenoble Cedex 9, France.

Crystallization of human insulin was performed using two phenolic derivatives, the organic ligands meta (m)-cresol and 4-nitrophenol and it was followed by structural characterization of the crystals that were obtained, at the level of unit cell symmetry and dimensions. Crystallization was achieved over a range of pH, in the presence of zinc ions, in order to study the behavior of insulin structures, which are observed under certain conditions.

The crystals that were acquired were exposed to Synchrotron X-ray radiation, at European synchrotron, ESRF, and at the Swiss synchrotron, SLS, in order to obtain high resolution diffraction patterns. The technique employed was the powder diffraction, which has been proven the past few years crucial for characterization of microcrystalline protein structures [1].

The diffraction data were processed with specific crystallography software (DASH, PRODD), in order to allow the identification of the crystalline phases which are distinguished on the basis of their structural characteristics [2].

Under acidic conditions (pH: 4.7- 6.5), with both ligands, we observe the emergence of a new crystal structure of monoclinic symmetry (space group: P2₁). In contrast, the alkaline environment (pH: 7.2- 8.50) promotes a known polymorph belonging in the rhombohedral symmetry (space group: R3). The configuration of the molecule, as it is indicated by the constants of the fundamental cell, varies between the R₆ form and the T₃R₃^f one.

The ultimate goal of this study is the possible application of the findings in the pharmaceutical treatment of diabetes mellitus, which is a result of failure / ineffectiveness of insulin. Moreover, the reproducibility of similar experiments was tested, verifying thereby, the structural stability of microcrystalline samples over the time.

[1] Von Dreele, R. B., *Methods Enzymol.* 2003, 368, 254 -267. [2] Margiolaki, I. & Wright, J. P., *Acta Cryst.* 2008, A64, 169 -180

Keywords: structural biology, macromolecular powder diffraction, insulin.

*Microsymposium MS04:
Combined Methods for Structure Analysis:
Electron diffraction, Powder diffraction & Tomography*

Chairs: Lynne McCusker, ETH Zurich (CH)

Carsten Gundlach, Technical University of Denmark (DK)

Microsymposium: Monday 16 June 2014 Afternoon – Chemistry AUD I, 1514-213

Poster session: Monday 16 June 2014 – Chemistry AUD VI, 1510-213

Keynote Lecturers:

MS04_K1

Combining X-ray powder diffraction and 3D imaging

[Christopher Egan^a](#), [Simon Jacques^a](#) & [Robert Cernik^a](#)

^aUniversity of Manchester, School of Materials, Manchester, UK, e-mail: christopher.egan@manchester.ac.uk

We present experimental techniques that combine X-ray powder diffraction with three dimensional (3D) imaging using high energy synchrotron radiation. Images contain powder diffraction patterns in every voxel, enabling physical and chemical properties of materials to be studied in 3D. We discuss scanning beam tomography utilising both angle-dispersive and energy-dispersive diffraction. We will also describe a new full-field X-ray diffraction radiography method which uses pixelated energy-dispersive detectors. With this system, each pixel of an area detector contains a powder diffraction pattern, so does not require beam scanning and can be combined with 3D tomography via sample rotation alone. Example applications of these methods will be presented covering biomaterials, catalysis and metallurgy.

- [1] Egan C.K. *et al.*, *Acta Biomater.* (2013) **9**, 8337-8345
[2] Lazzari O. *et al.*, *J. Synchrotron Rad.* (2012) **19**, 471-477
[3] Egan C.K. *et al.*, *Proc. R. Soc. A* (2014) **470**, 20130629

Keywords: XRD, tomography, energy-dispersive detectors, materials characterisation

MS04_K2

A comparative study of Pd₂Ga/SiO₂: in situ X-ray Diffraction and Electron Microscopy

[E. M. Fiordaliso^a](#), [I. Sharafutdinov^b](#), [J. Kehres^b](#), [C. Gundlach^c](#), [D. Thomas^d](#), [T. W. Hansen^a](#), [I. Chorkendorff^{cb}](#), [J. B. Wagner^a](#) & [C. D. Damsgaard^{a,b}](#)

^aCenter for Electron Nanoscopy, Technical University of Denmark, DK-2800 Lyngby, Denmark

^bCenter for Individual Nanoparticle Functionality, Department of Physics, Technical University of Denmark, DK-2800 Lyngby, Denmark

^cDepartment of Physics, Technical University of Denmark, DK-2800 Lyngby, Denmark

^dMax IV laboratory, University of Lund, SE-22100 Lund, Sweden

e-mail: e.fiordaliso@cen.dtu.dk

Complementary *in situ* characterizations techniques such as *in situ* X-ray Diffraction (XRD) and Environmental TEM (ETEM) are invaluable tools for studying the life cycle of heterogeneous catalysts [1]. Pd-Ga intermetallics have recently been investigated for several catalytic reactions including hydrogenation of acetylene [2], steam reforming of methanol [3] and methanol synthesis from CO₂/H₂ [4,5]. In this study, a Pd₂Ga/SiO₂ catalyst is characterized during nanoparticle formation and CO₂ hydrogenation to methanol at ambient pressure. *In situ* XRD is used to investigate the phase at four stages along the catalyst life cycle, i.e. drying, calcination, reduction, and methanol synthesis. The measurements are carried out using an Anton Paar XRK-900 furnace cell connected to a gas handling system and a PANAnalytical X'PERT PRO diffractometer. XRD patterns reveal the PdO crystallographic phase of the catalyst during drying and calcination, as shown in Fig. 1 (a). No distinct peaks are observed for Ga and Ga₂O₃, indicating amorphous gallium compounds. The Pd₂Ga phase is formed upon reduction and is stable during methanol synthesis, as shown in Fig. 1 (b). TEM images acquired with a Tecnai TEM (FEI) operated 200 kV show particle formation upon calcination, which determine the distribution of the Pd₂Ga nanoparticles formed during reduction. ETEM images and diffraction patterns (DP) are acquired along the catalyst life cycle with an Environmental Titan TEM (FEI) operating at 300 kV and at 4 mbar gas mixtures. The radial intensity profiles obtained from the DPs are shown in Fig. 2. The images and the DPs are consistent with the *ex situ* images and with the XRD patterns, indicating a negligible pressure dependence of nanoparticle and active phase formation. Atomic resolved images and STEM-EELS spectra are acquired from individual Pd₂Ga nanoparticles at the ETEM under reduction conditions.

- [1] Hansen *et al.*, *Journal of Materials Science & Technology* 26 (2010) (11), 1338.

- [2] J. Osswald *et al.*, *Journal of Catalysis* 258 (2008) 210. [3] S. Penner *et al.*, *Applied Catalysis A* 358 (2009) 193. [4] S. E. Collins *et al.*, *Journal of Catalysis* 292 (2012) 90. [5] A. L. Bonivardi *et al.*, *Studies in Surface Science and Catalysis* 130 (2000) 3747.

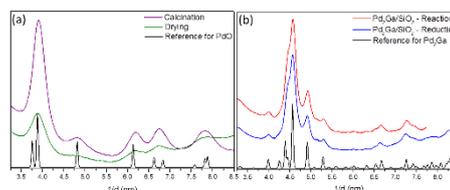


Fig. 1. (a) XRD patterns of the Pd₂Ga/SiO₂ catalyst acquired at 1 bar air after drying (120°C) and calcination (260°C). (b) XRD patterns acquired at 1 bar after reduction (H₂, 550°C) and methanol synthesis (H₂+CO₂, 200°C).

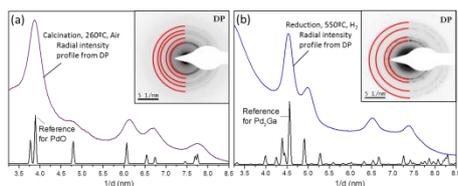


Fig. 2. Radial intensity profiles from diffraction patterns of Pd₂Ga/SiO₂ acquired at the ETEM at 4 mbar during (a) calcination (air, 260°C) and (b) reduction (H₂, 550°C).

Keywords: In situ XRD, ETEM, Electron diffraction, Pd₂Ga, particle formation, methanol synthesis

Oral Presentations:

MS04_O1

Reveal the crystal structure of nano-size microporous materials by combining RED and PXRD

Hong Chen, Fei Peng & Junliang Sun

Department of Materials and Environmental Chemistry, Stockholm University, Sweden

Inorganic microporous materials such as zeolites, phosphates, germanates, borates are of great interest due to their diversity pores and properties^[1-6]. The crystal structure of these types of materials is the key factor for understanding their actual performance. However, most of these types of materials are crystallized in nano-size crystals, which make the structure determination of these kinds of materials as a big challenge for conventional single crystal X-ray diffraction techniques. Here by using the home developed rotation electron diffraction (RED) technique^[7] for data collection together with ab-initio structure solution algorithm such as direct methods in SIR2011^[8], we managed to solve the crystal structure model for three different types of nano-sized microporous materials, further combing with Rietveld refinement on Powder X-ray diffraction (PXRD), their final structure model can be accomplished. The first materials is a germanosilicate zeolite with a three-dimensional 11×11×12-ring channel system denoted as PKU-16 (PKU, Peking University)^[9]. The 3D reciprocal lattice reconstructed from the RED dataset shows it with a tetragonal unit cell of a ~ 19.04 Å and c ~ 11.73 Å. All Si/Ge and part of oxygen atoms were located directly with the P42/mnm symmetry, and the rest oxygen atoms were then found from residue peaks. The framework atoms could be refined anisotropically without any restraints by SHELX97^[10]. A combined study by Rietveld refinement on PXRD and force field simulation resulted in disordered OSDAs in the pores. The three-dimensional 11×11×12-ring channel system is shown in this structure. The second sample is an aluminoborate sample, RED data shows it crystallized in hexagonal unit cell with a ~ 14.58 Å and c ~ 12.45 Å, the framework atoms can be directly located with P-3c based on the RED data and refined anisotropically without any restraints by SHELX97. Rietveld refinement on PXRD can fatherly helpful on locating the boric acid in the channels. One dimensional 12-ring is shown in this structure. The third sample is an as-synthesized aluminophosphate multiple phases sample; two different nano-size crystals with different morphologies were shown in the sample. Although a lot of synthesis experiments were performed in order to

achieve the pure phase samples, the pure phase sample for neither of these two phases has achieved yet. RED data shows that both of these two phases are quite stable under electron beam. The complete structure models for these two phases can be directly obtained against RED data. Phase 1 shows a layered aluminophosphate structure, and phase 2 shows one dimensional 7-ring channel structure.

-
- [1] M. E. Davis, *Nature* **2002**, *417*, 813–821.
[2] A. K. Inge, S. Huang, H. Chen, F. Moraga, J. Sun, X. Zou, *Cryst. Growth Des.* **2012**, *12*, 4853–4860.
[3] L. Liu, Z.-B. Yu, H. Chen, Y. Deng, B.-L. Lee, J. Sun, *Cryst. Growth Des.* **2013**, *13*, 4168–4171.
[4] H.-Y. Lin, C.-Y. Chin, H.-L. Huang, W.-Y. Huang, M.-J. Sie, L.-H. Huang, Y.-H. Lee, C.-H. Lin, K.-H. Lii, X. Bu, et al., *Science* **2013**, *339*, 811–813.
[5] H. Chen, Y. Deng, Z. Yu, H. Zhao, Q. Yao, X. Zou, J. Sun, *Chem. Mater.* **2013**, *25*, 5031–5036.
[6] H. Chen, Z. Yu, Z. Bacsik, H. Zhao, Q. Yao, J. Sun, *Angew. Chem. Int. Ed. Engl.* **2014**, DOI: 10.1002/anie.201311122.
[7] W. Wan, J. Sun, J. Su, S. Hovmo, *J. Appl. Crystallogr.* **2013**, *46*, 1863–1873.
[8] M. C. Burla, R. Caliendo, M. Camalli, B. Carrozzini, G. L. Casciarano, C. Giacovazzo, M. Mallamo, A. Mazzone, G. Polidori, R. Spagna, *J. Appl. Crystallogr.* **2012**, *45*, 357–361.
[9] W. Hua, H. Chen, Z. Yu, X. Zou, J. Lin, J. Sun, *Angew. Chem. Int. Ed. Engl.* **2014**, 10.1002/anie.201309766.
[10] G. M. Sheldrick, *Acta Crystallogr. A* **2008**, *64*, 112–122.

Keywords: Rotation electron diffraction, Rietveld refinement, Powder X-ray diffraction, Structure determination

MS04_O2

Compact Bone Studied by Diffraction Tomography

[Mie Birkbak^a](#), [Simon Frølich^a](#), [Hanna Leemreize^a](#), [Stuart R Stock^b](#) & [Henrik Birkedal^a](#)

^aAarhus University, Denmark,
^bNorthwestern University, USA,
e-mail: hbirkedal@chem.au.dk

There is a strong need for improving our understanding of complex multiphase materials. One approach that meets this challenge is diffraction tomography. Herein we describe the application of diffraction tomography to study compact bone.

Bone is a highly complex material, consisting of 7 hierarchical levels. On the smallest length scale bone is built of plate shaped inorganic nanoparticles in an organic phase, primarily collagen type I. In order to study structures with both highly complex spatial organization and phase distribution we need imaging techniques capable of distinguish these features in 3D.

Moreover many specific scientific questions concerns sub-volumes buried within the sample and to access these we need a nondestructive technique capable of penetrating large sample volumes. Computed tomography (CT) utilizes mathematical algorithms to reconstruct a 3D model from several x-ray projections recorded at different angles. However, CT traditionally only yields information on X-ray absorption. In order to obtain a full understanding of complex samples, much more complex contrast mechanisms are needed. X-ray crystallography provides a wealth of information on the microstructural nature and identity of all phases in a given sample. However, these data describe only the average properties of the illuminated volumes. Here we describe how x-ray crystallography and computed tomography can be united to produce information dense maps of complex samples in 3D using crystallographic information as contrast.¹⁻³

We have applied the technique to bovine compact bone. Bone rods have been cut out in 1×1 mm² rods both along and perpendicular to the long bone axis. Diffraction data collected at high X-ray energies (52 keV) at beamline 1-ID at APS were used for analysis. Since diffraction tomography delivers information on a wealth of parameters simultaneously in one experiment without destroying the sample, the technique is ideal to follow structural development in samples under applied stimuli e.g. load.

-
- [1] P. Bleuet, E. Welcomme, E. Dooryhée, J. Susini, J. L. Hodeau & P. Walter, *Nature Materials*, 2008, *7*, 468–472.
[2] H. Leemreize, J. D. Almer, S. R. Stock and H. Birkedal, *Journal of the Royal Society Interface*, 2013, *10*, no. 86
[3] S. R. Stock, F. de Carlo, J. D. Almer, *Journal of Structural Biology*, 2008, *161*, 144–150

Keywords: Diffraction Tomography, Bone, hierarchical materials

MS04_O3

Study of high temperature transformation of titanate nanotubes

[Tereza Brunátová^a](#), [Zdenek Matěj^a](#), [Peter Oleynikov^b](#), [Stanislav Daniš^a](#), [Daniela Popelková^c](#) & [Radomir Kužel^a](#)

^aCharles University, Faculty of Mathematics and Physics, Dept. of Condensed Matter Physics,

Prague, Czech Republic,

^bStockholm University, Dept. of Materials and Environmental Chemistry, Stockholm University,

SE-106 91 Stockholm, Sweden,

^cInstitute of Macromolecular Chemistry, Academy of Sciences of the Czech Republic, Prague, Czech Republic

Study of temperature stability of titanate nanotubes (Ti-NT) is of interest because some possible applications require heating [1]. At high temperatures titania nanowires are obtained. Similarly to Ti-NT several possible phases of titanate/titania nanowires/ nanorods can be found as for example: $\text{Na}_2\text{Ti}_6\text{O}_{13}$ [2], $\text{Na}_2\text{Ti}_3\text{O}_7$ [2], rutile phase of TiO_2 [2-4], anatase phase of TiO_2 [2], [3], beta TiO_2 [4]. The final structure depends also on the amount of sodium ions, if they are present in original Ti-NT sample.

In this contribution, the structure of titanate nanorods and titania nanowires was studied. The structure of titanate nanorods was determined by combination of powder X-ray diffraction and 3D precession electron diffraction. The titanate nanorods were prepared by heating of titanate nanotubes up to 850 °C in air atmosphere. Two kind of particles were found in heated sample- nanorods and nanoparticles. The nanorods possess the structure of $\text{Na}_2\text{Ti}_6\text{O}_{13}$ whereas the nanoparticles show the structure of the phases of TiO_2 - anatase and rutile. Titania nanowires were obtained from titanate nanotubes by heating in vacuum atmosphere at 900 °C. The structure of nanowires was studied by X-ray diffraction. The diffraction data were evaluated by the total powder pattern fitting method by the program MStruct [5]. The structure of nanowires was identified as anatase phase of TiO_2 . A new model of crystallite shape function was added into MStruct package in order to properly simulate the diffraction pattern from nanorods. Three different models were used – model of spherical nanoparticles, spherical base nanorods and nanorods with elliptical base and the best match was obtained for the model of elliptical base nanorods.

-
- [1] Bavykin D. V., Walsh F. C.: Titanate and Titania Nanotubes: Synthesis, Properties and Applications, RSC Publishing, 2010.
 [2] Morgado E., jr, de Abreu M. A. S., Pravia O. R. C., Marinkovic B. A., Jardim P. M., Rizzo R.C., Araujo A.S., *Solid State Science*, 2006, 8, 888-900
 [3] Yu J., Yu H., Cheng B., Trapalis C., *Journal of Molecular Catalysis A*, 2006, 249, 135-142.
 [4] Suzuki Y., Yoshikawa S., *Journal Material Res.*, 2004, 19, 982-985.
 [5] Matěj Z., Kužel. R., Nichtova L., *Powder Diffraction*, 2010, 25, 125-131.

Keywords: Titanate nanorods, titania nanowires, high-temperature transformation

Structure analysis from powder having a strong anisotropic shape using a Gandolfi camera

A. Ohbuchi, Y. Shiramata, T. Konya, A. Yamano & G. Fujinawa

Rigaku Corporation, Tokyo 196-8666, Japan,
 E-mail: a-obuchi@rigaku.co.jp

Powder X-ray diffraction data with accurate diffraction intensities and diffraction positions must be obtained to perform crystal structure analysis. To meet these requirements, the sample is usually enclosed in a capillary. However, when the sample possesses preferred orientation, accurate diffraction intensities can't be obtained. In this case, the capillary is rotated to suppress effects of preferred orientation. However, when the sample has severe preferred orientation due to its crystal habit such as having a strong anisotropic shape, sometimes rotating the sample enclosed in a capillary not sufficient to exclude errors in intensity.

In this study, Bismuth oxychloride presenting strong preferred orientation was analyzed using a Gandolfi camera in addition to a capillary attachment on a multipurpose X-ray diffraction system, SmartLab equipped with a two-dimensional detector. The PDXL package was used for crystal structure analysis.

Bismuth oxychloride was analyzed first using a capillary attachment only. However the crystal structure analysis couldn't be conducted because of crystal habit (Fig. 1). Then the shape of crystallite of bismuth oxychloride was analyzed by the Rietveld refinement using the FP method. It was found that the crystallite had a disk-like shape. Crystal structure analysis of a sample possessing such a strong crystal habit is difficult even if a capillary attachment is used. Therefore, a Gandolfi camera was employed in combination with the capillary attachment. Usually, a Gandolfi camera is used to obtain powder diffraction data from a single crystal or a small agglomerate of single crystals.

A Gandolfi camera has 2 rotation axes: a sample spin axis fixed at 45 ° to the base and the rotation axis of the base itself. Result of crystal structure analysis of a bismuth oxychloride was shown Fig. 2. Residuals

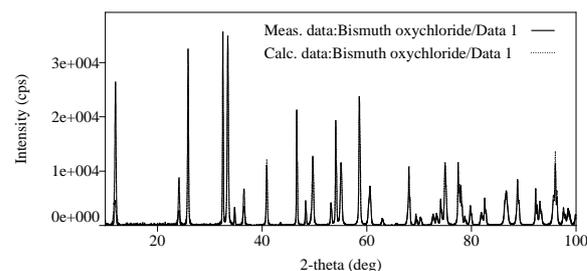


Fig. 1 Observed (solid line) and calculated (dotted line) diffraction patterns and with Rietveld refinement using a capillary attachment.

between observed and calculated diffraction pattern were sufficiently small.

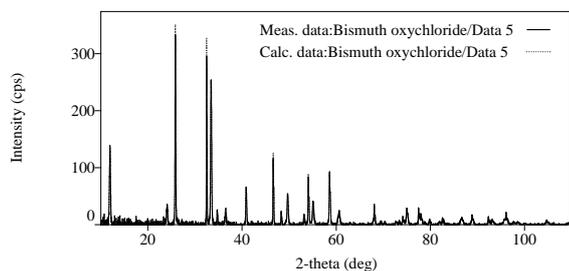


Fig. 2 Observed (solid line) and calculated (dotted line) diffraction patterns and with Rietveld refinement using a Gandolfi camera.

Keywords: Gandolfi camera, anisotropic shape, two-dimensional detector, Rietveld refinement

Posters:

MS04_P31

Structure of thin film TiO₂ grown by magnetron sputtering analyzed by ion, electron, and X-ray scattering

[K. A. Janik^a](#), [B. Seger^b](#), [M. B. Sillassen^c](#), [C. D. Damsgaard^{a,b}](#),
[I. Chorkendorff^b](#) & [J. B. Wagner^a](#)

^a Center for Electron Nanoscopy, Technical University of Denmark, 2800 Kongens Lyngby, Denmark

^b Department of Physics, Technical University of Denmark, 2800 Kongens Lyngby, Denmark

^c Interdisciplinary Nanoscience Center and the Department of Physics, Aarhus University, 8000 Aarhus, Denmark

Titanium dioxide (TiO₂) receives a lot of attention in the context of hydrogen production by photocatalytic water splitting, where TiO₂ can be used as a layer protecting silicon photocathodes. For this application, the TiO₂ material is synthesized by the physical vapor deposition (PVD) in form of thin films. The overall structural quality of the TiO₂ films, and thereby their properties, depends on the PVD processing conditions. Hence, our study focuses on getting a clear insight into films' structure by comprehensive description of compositional, morphological, and crystallographic aspects of such deposits. A set of techniques that employ ion, electron and X-ray scattering is used for this purpose.

This work presents an example of structural characterization of a TiO_x deposit grown on Si <001> by reactive DC magnetron sputtering from a metal titanium (Ti) target in an Ar/O₂ gas mixture. Rutherford backscattering spectrometry indicates that the TiO_x film is close to the stoichiometric compound, i.e. TiO₂. X-ray diffraction performed in the symmetric (θ - 2θ) and asymmetric (ω - 2θ) scans shows that the film is polycrystalline and composed of two crystallographic phases, i.e. rutile and anatase. As revealed by scanning electron microscopy (SEM), the deposit is characterized by columnar grains. The crystallinity and morphology of the deposit is further studied by electron diffraction (ED) and transmission electron microscopy (TEM). TEM and ED measurements are performed on thin focused ion beam (FIB) milled lamellas prepared in the direction parallel and perpendicular to the direction of the TiO₂ film growth.

Keywords: titanium dioxide, Rutherford backscattering, electron diffraction, X-ray diffraction, grazing incidence X-ray diffraction

MS04_P32

Chemical preparation, crystallographic characterization and vibrational study of two new condensed phosphates

A. Kheireddine^{a*}, M. Tridane^{a,b}, I. Fahim^a, H. Moutaabbid^c,
M. Moutaabbid^a, A. Charaf^a, M. Radid^a, F. Salhamen^a, S.
Benmokhtar^a & S. Belaouad^{a*}

^a Laboratoire de Chimie-Physique des Matériaux,

Faculté des Sciences Ben M'sik, B. P. 7955. Casablanca. Maroc.

^b Centre Régional des métiers d'enseignement et de formation Casablanca Anfa
Bd Bir Anzarane Casablanca. Maroc.

^c Institut de minéralogie et de physique des milieux condensés (IMPMC).
CNRS : UMR 7590 – IPG PARIS – Université Pierre et Marie Curie (UPMC) –
Paris VI – Université Paris VII – Paris Diderot

* Corresponding author's e-mail : kheireddine.azi@gmail.com
belaouad.s@gmail.com

Chemical preparation, crystallographic characterization and vibrational studies are reported for two new condensed phosphates associated to nickel-rubidium $\text{NiRb}_4(\text{P}_3\text{O}_9)_2$ and strontium-thallium $\text{SrTl}_4(\text{P}_3\text{O}_9)_2$. $\text{SrTl}_4(\text{P}_3\text{O}_9)_2$ was prepared by the method of ion-exchange resin and $\text{NiRb}_4(\text{P}_3\text{O}_9)_2$ was obtained by total thermal dehydration of $\text{NiRb}_4(\text{P}_3\text{O}_9)_2 \cdot 6\text{H}_2\text{O}$. $\text{SrTl}_4(\text{P}_3\text{O}_9)_2$ is rhombohedral, $Z = 2$, space group $P\bar{3}_1c$, with the following unit-cell parameters: $a = 7,424(1) \text{ \AA}$, $c = 20,176(2) \text{ \AA}$ and $V = 2807.46(2) (\text{ \AA}^3)$. $\text{NiRb}_4(\text{P}_3\text{O}_9)_2$ is triclinic, $Z = 2$, space group $P\bar{1}$, with the following unit-cell parameters: $a = 8,046(9) \text{ \AA}$, $b = 9,733(0) \text{ \AA}$, $c = 4,327(5) \text{ \AA}$, $\alpha = 98.053^\circ$, $\beta = 88.616^\circ$, $\gamma = 84.761^\circ$ and $V = 333,95(2) (\text{ \AA}^3)$. Vibrational study is also reported for the title compounds

Keywords: chemical preparation, crystallographic characterization, infrared spectrometry, condensed phosphate, $\text{SrTl}_4(\text{P}_3\text{O}_9)_2$, $\text{NiRb}_4(\text{P}_3\text{O}_9)_2$, P_3O_{93-} ion, XRD, IR.

MS04_P33

Combined XRD and XPS analysis of in-situ plasma hydrogenated magnetron sputtered Mg films

Martynas Lelis^a, Marius Urbonavicius^a & Darius Milcius^a

^aLithuanian Energy Institute, Lithuania, ml@mail.lei.lt

Contrary to traditional methods including top layer catalyst deposition and ex-situ hydrogenation in current study Mg-H films were synthesised using magnetron sputtering in Ar+ atmosphere and their "in-situ" hydrogenation in magnetron induced hydrogen plasma.

XRD analysis of hydrided Mg-H films revealed changes in preferred orientation of the films and varying kinetics of crystalline MgH₂ phase formation on different substrates. The appearance of significant amount of crystalline MgH₂ phase after prolonged time of "in-situ" hydrogenation presupposed that samples without clear expression of MgH₂ crystal phase had hydrogen rich amorphous Mg phase which is not observable by XRD. The analysis of predicted hydrogen containing phase was performed using combination of conventional XRD, GIXD and XPS analysis technique which was suggested by Friederichs et. al. [1]. The obtained data of hydrogen containing phase distribution at the surface of the samples and its distribution depth profiles are presented together with considerations related to the efficiency of the proposed hydrogenation and combined analysis methods.

[1] O. Friedrichs, J.C. Sánchez-López, C. López-Cartes, M. Dornheim, T. Klassen, R. Bormann, A. Fernández, *Applied Surface Science*. 2006, Vol. 252, pages 2334–2345

Keywords: MgH₂, plasma, thin films, in-situ hydrogenation, XRD, XPS

MS04_P34

Structure determination of La(Nb,Ti)₅O₁₃ ceramic using X-ray and neutron powder diffraction and DFT calculations

Anton Meden^a, Katarina Stare^a, Jernej Stare^b, Radovan Černý^c, Sreco Skapin^d & Danilo suvorov^d

^aUniversity of Ljubljana, Faculty of Chemistry and Chemical Technology, Ljubljana, Slovenia

^bNational Institute of Chemistry, Ljubljana, Slovenia

^cUniversité de Geneve, Geneve, Switzerland

^dJozef Stefan Institute, Ljubljana, Slovenia
e-mail: tone.meden@fkt.uni-lj.si

A previously unknown phase has been identified in the La₂O₃-TiO₂-Nb₂O₅ (LNT) system. The formula, determined by EDS, was La_{0.946}Nb_{3.162}Ti_{1.838}O₁₃. The synchrotron powder pattern was successfully indexed and revealed a triclinic unit cell: $a=7.328$, $b=7.417$, $c=10.672 \text{ \AA}$, $\alpha=84.13$, $\beta=80.07$, $\gamma=60.41^\circ$. Structure was solved by Fox [1] and validated by successful combined X-ray and neutron Rietveld refinement.

Detailed structural characterization of the material, related to the crystallographic site preferences by Ti and Nb atoms was assisted by periodic quantum chemical calculations. We used Density Functional Theory methods to study relative stability of the possible isomers with different Ti and Nb distributions in the structure. We were able to deduce the thermodynamic

site preference of titanium and niobium over the five crystallographic sites. The model structure undertaken in this study had a formula $\text{LaNb}_3\text{Ti}_2\text{O}_{13}$ and gives ten site-isomers where two titanium and three niobium atoms occupy the five available sites. All the isomers were subjected to geometry optimization. The relative energies of isomers are in good agreement with the refined occupancies of sites. The optimized structures, particularly of the energetically favored isomers, match fairly well the diffraction-determined geometry. The overall agreement between theoretical calculations and experimental data justifies the use of quantum chemical methods and proves them being reliable and promising complementary tools for the structural studies of ceramic materials.

[1] Favre-Nicolin V; Černý R, *J. Appl. Cryst.* 2002, **35**, 734-743.

Keywords: La-Nb-Ti-O ceramic, Structure solution, DFT calculation

Microsymposium MS05: Energy Materials

Chairs: Bill David, ISIS Facility (UK)

Dorthe Bomholt Ravnsbæk, Aarhus University (DK)

Microsymposium: Wednesday 18 June 2014 Afternoon – Chemistry AUD I, 1514-213

Poster session: Monday 16 June 2014 – Chemistry AUD VI, 1510-213

MS05_K1

Powder Diffraction Studies of Metal Hydrides Proposed for Concentrated Solar Thermal Energy Storage Applications

[Craig E. Buckley](#), [Drew A. Sheppard](#), [Mark Paskevicius](#) & [Tam Nguyen](#)

Department of Imaging and Applied Physics, Fuels and Energy Technology Institute, Curtin University, Perth, WA, Australia, e-mail: C.Buckley@curtin.edu.au

Solar energy is the most abundant renewable energy resource that is available and therefore logically represents the most important renewable energy resource to be focused upon. The IEA roadmap for solar energy set a target of ca. 22% of global electricity production from solar energy by 2050, with 50% being produced from concentrating solar thermal power systems. Achieving this target will be possible only if the costs of producing electricity from solar energy are significantly reduced and cost effective energy storage technologies can be developed. A major challenge is to achieve continuous, low-variability power generation from renewable energy sources, for stand-alone applications or for integration with domestic power grids. Solar mirror collection fields can collect thermal energy during the day and run a heat engine to convert it into electricity, but cannot provide power at night. However, if some of the heat is used to remove hydrogen from a metal hydride, the reverse reaction where hydrogen absorbs back into the metal hydride can then occur at night, releasing heat for power generation. This allows solar energy to provide 24 hour power generation. By combining a high temperature metal hydride with a low temperature metal hydride a coupled pair reversible metal hydride thermochemical solar energy storage system is created [1 - 3]. Concentrated solar thermal coupled to a high and low temperature metal hydride has the potential to provide a continuous supply of electricity to remote areas in Australia and the World. I will present powder diffraction results on some of the hydride materials proposed as being suitable for concentrated solar thermal applications

[1] D.N. Harries, M. Paskevicius, D.A. Sheppard, T.E.C. Price, C.E. Buckley. *Proc. of the IEEE*, (2012) **100**, 539.

[2] M. Fellet, *Feature Editors*: C.E. Buckley, M. Paskevicius, D.A. Sheppard. *MRS Bulletin* (2013) **38**, 1012.

[3] D.A. Sheppard, M. Paskevicius, C.E. Buckley. *Chemistry of Materials*, (2011) **23**, 4298.

Keywords: Solar thermal, hydrogen, energy storage, powder diffraction

Watching nanocrystals form

[Bo Brummstedt Iversen](#)

Centre for Materials Crystallography, Department of Chemistry and iNANO, Aarhus University, DK-8000 Århus C, Denmark, bo@chem.au.dk

Reactions in steel containers under solvo/hydrothermal conditions are widely used to produce crystalline nanoparticles. The solvo/hydrothermal approach often provides excellent control over nanoparticle characteristics such as size, size distribution, morphology and crystallinity. However, most progress in the solvothermal field is empirical in nature. Recent development of in situ X-ray scattering techniques now allow real time monitoring of the formation of nanoparticles under high pressure, high temperature conditions, and this opens up the possibility for synthesizing nanoparticles by design. We have developed unique in situ reactors for studies of reactions in sub- and supercritical fluids [1]. By means of Small Angle X-ray Scattering (SAXS), Wide Angle X-ray Scattering (WAXS), Total scattering and EXAFS we have obtained knowledge on the formation and growth of a range of important nanoparticles all the way from the precursor structures to the final crystalline product. text of the abstract should be placed here (Times New Roman 8, Justified, Single-spaced).

[1] (a) Jensen et al., *Angew. Chem. Int. Ed.* 2007, 46, 1113; (b) Bremholm et al., *Angew Chem. Int. Ed.* 2009, 48, 4788; (c) Lock et al., *Angew Chem. Int. Ed.* 2011, 50, 7045; (d) Jensen et al., *J. Am. Chem. Soc.* 2012, 134, 6785; (e) Tyrsted et al., *Angew. Chem. Int. Ed.* 2012, 51, 9030; (f) Saha et al., *Angew. Chem. Int. Ed.* 2014, 53, 3667; (g) Tyrsted et al., *IUCr-J* 2014, 1, doi:10.1107/S2052252514006538

Keywords: in situ, nanocrystals, total scattering, powder diffraction, solvothermal synthesis

MS05_O1

Decomposition Pathways of Complex Hydrides with Metal Sulphides

Mark Paskevicius^{a,b}, Drew A. Sheppard^a, Lars H. Jepsen^b,
Petra A. Szilágyi^a, Tam Nguyen^a, Torben R. Jensen^b & Craig
E. Buckley^a

^aDepartment of Imaging and Applied Physics Curtin University, Australia.
^bInterdisciplinary Nanoscience Center (iNANO), Aarhus University, Denmark.
e-mail: mark.paskevicius@gmail.com

Hydrogen is considered to be a key future energy carrier but its safe, compact and efficient storage are one of the key barriers to its widespread use. Hydrogen can be stored in the solid state using complex metal hydrides, where the hydrogen is covalently bonded in complex anions such as AlH_4^{-1} , AlH_6^{-3} , BH_4^{-1} and NH_2^{-1} . However, none of the known complex hydrides currently satisfy the requirements for near ambient temperature hydrogen storage and entail the disadvantages of: multiple hydrogen release steps, high temperature hydrogen release and a lack of reversibility.

Results on NaAlH_4 mixed with aluminium sulphide [1] showed unexpectedly complex decomposition behaviour by *in-situ* powder diffraction, revealing 6 new phases forming and decomposing during heating to 400°C. We have since extended our study to the reactions between other complex hydrides with a range of metal sulphides to investigate the wealth of new reaction pathways that can occur during hydrogen release. Many currently unknown compounds can be found in this new class of materials, which can be explored for their potential as hydrogen storage materials.

[1] D.A. Sheppard, L.H. Jepsen, T.R. Jensen, M. Paskevicius, C.E. Buckley, *J. Mater. Chem. A*. 2013, 1, 12775-12781

Keywords: Hydrogen Storage, *in-situ* Powder Diffraction, Thermal Decomposition

Thermodynamics and Crystal Structures of the Alkali Silanides MSiH_3 (M=K, Rb, Cs)

Jean-Noël Chotard^{a*}, Wan Si Tang^a, Pascal Raybaud^b &
Raphaël Janot^a

^aLaboratoire de Réactivité et Chimie des Solides (LRCS), UMR 7314
CNRS, Université de Picardie Jules Verne, 33 rue Saint-Leu, 80039 Amiens
Cedex, France

^bIFP Energies nouvelles, Rond-point de l'échangeur de Solaize BP 3, 69360
Solaize, France, e-mail: jean-noel.chotard@u-picardie.fr

Following our work on the direct hydrogenation of Zintl phase KSi [1] leading to the reversible alkali silanide $\alpha\text{-KSiH}_3$, we extended our investigation to the thermodynamic stability and crystal structures of the other MSiH_3 alkali silanides (M=Rb, Cs) using combined experimental and theoretical studies. Under mild conditions (*ca* 50 bar H_2 at 100°C) MSi Zintl phases (M=K, Rb, Cs) can absorb 3 H/f.u. corresponding to hydrogen contents of 4.3, 2.6 and 1.85 wt% H_2 , respectively.

With the three alkali metals, a structural transition between a high ($\alpha\text{-MSiH}_3$) and a low temperature form ($\beta\text{-MSiH}_3$) is observed around 270 K. The complete crystal structures of those six phases have been fully solved using neutron powder diffraction (NPD) on deuterated samples [2]. For the first time, the crystal structures of $\beta\text{-RbSiH}_3$ and $\beta\text{-CsSiH}_3$ are reported showing a monoclinic distortion of the $\beta\text{-KSiH}_3$ orthorhombic unit cell. The Si-H bonding in the α - and $\beta\text{-MSiH}_3$ phases will be detailed thanks to the NPD results as well as infrared spectroscopy. The temperature-dependency of the $[\text{SiH}_3]^-$ anionic group mobility will be especially discussed in correlation with the unusual thermodynamic properties encountered for the $\text{MSi}/\alpha\text{-MSiH}_3$ equilibrium.

[1] J.-N. Chotard, W.S. Tang, P. Raybaud, R. Janot, *Chem. Eur. J.* 17 (2011) 12302

[2] W.S. Tang, J.-N. Chotard, P. Raybaud, R. Janot, *J. Phys. Chem. C*, in press, dx.doi.org/10.1021/jp411314w

Keywords: Powder Neutron Diffraction, Hydrogen storage, silanides, thermodynamic

MS05_O3

Borohydrides: in situ powder diffraction and Li-rich topologies

Radovan Černý, Pascal Schouwink & Yolanda Sadikin

University of Geneva, Switzerland,
e-mail: Radovan.Cerny@unige.ch

Metal borohydride systems are of interest due to their potential as hydrogen storage materials, solid state electrolytes in batteries and as novel hydridic frameworks. Crystal structures range from packed predominantly ionic compounds characteristic of *e.g.* the alkali-metal borohydrides, to 3-dimensional frameworks as well as nano-porous frameworks found amongst the alkaline-earth metal borohydrides. For reasons of gravimetric capacity it is desirable to build hydrogen storage materials from the lightest possible metal cations and the lightest possible anion with the highest hydrogen content. For battery application the cation mobility is the key parameter. The interest in the Li-BH₄ system is therefore eminent.

We will demonstrate by applying the principles of topological analysis and coordination chemistry that the Li⁺ cation is a highly versatile component when it is used to construct negatively charged Li-BH₄ nets counter-balanced by larger cations in bi- or tri-metallic compounds. A wide spectrum of stoichiometries and connectivities results. In the Li-Cs-BH₄ system the topologies range from single chains up to frameworks with 3 types of coordination mode of the Li node, and connectivities that are rarely observed amongst oxides, for instance tetrahedral edge sharing [1]. We will also show which topologies of the Li-BH₄ nets favor high Li⁺ mobility.

The trimetallic K-Li-Mg-BH₄ presents an example that binary eutectic melting borohydride systems such as LiBH₄ - Mg(BH₄)₂, highly interesting from a gravimetric point of view, but not forming stable charge-balanced bimetallic compounds may be stabilized as a substructure by larger counter-cations in trimetallic systems [2]. Tentative ideas are suggested to make use of charged frameworks in synthetic approaches resembling those used to prepare zeolite-type compounds.

We will also discuss the first application of *in situ* ball milling [3] to complex hydride systems and show that the excellent time resolution (5 s) can reveal reaction pathways during mechano-chemical synthesis that are hardly understood from the post-milled analysis.

In situ powder diffraction with external stimuli temperature or milling time, consistently supported by *ab initio* calculations in the solid state, and together

with topological analysis allows to access structural details of increasing complexity.

[1] P. Schouwink *et al.*, (2014), in preparation. [2] P. Schouwink *et al.*, *Dalton Transactions* (2014), accepted. [3] T. Friščič *et al.* *Nature Chemistry*, (2013), 66-73.

Keywords: borohydride, hydrogen storage, solid state electrolyte

MS05_O4

Transition Metal Based Catalysts for Ammonia Decomposition

Claudia Weidenthaler^a, Valeria Tagliazucca^b, Matteo Leoni^c & Chun-Jiang Jia^d

^aMax-Planck-Institut für Kohlenforschung, Germany,
^bInstitute of Materials Chemistry Vienna University of Technology, Austria,
^cDepartment of Civil, Environmental and Mechanical Engineering, University of Trento, Italy, ^dSchool of Chemistry and Chemical Engineering, Shandong University, China
Claudia.weidenthaler@mpi-mail.mpg.de

Ammonia is an excellent hydrogen carrier and the decomposition of ammonia would be an elegant way to generate hydrogen for fuel cell applications without formation of CO_x. Alternatively, ammonia can be used directly as feed for solid-oxide fuel cells. Different transition metal catalysts have been investigated as potential catalysts for direct ammonia decomposition. Crystallographic studies with respect to phase changes, crystal structure variations, and microstructure properties have been performed. The behavior of the different catalysts has been investigated by *in situ* X-ray diffraction experiments under reaction condition. These results were directly correlated to the catalytic activity [1].

While several transition metal oxide catalysts reduce during the reaction with ammonia, others form nitrides. Some catalysts show significant changes of the chemical composition of the nitrides which leads to significant structure changes [2]. On the other hand, also changes of the microstructure properties of the catalyst in terms of domains size or defect variations influence the catalytic activity. The molybdenum nitride system is a very good example that various factors govern activity. Not only structure changes also changes of domain sizes and with this of specific surface areas, as well as defect concentrations have to be considered [1].

[1] Tagliazucca, V.; Schlichte, K.; Schüth, F.; Weidenthaler, C., *J. Catal.* 2013, 305, 277. [2] Tagliazucca, V. Leoni, M.; Weidenthaler, C.; *Phys. Chem. Chem. Phys.* 2014, 16(13), 6182.

Keywords: Ammonia decomposition, catalysis, *in situ* diffraction

Posters:

MS05_P35

Studies of antimony anode materials in sodium-ion batteries using in situ pair distribution function analysis and solid-state NMR.

Phoebe K. Allan^{a,b}, John M. Griffin^a, Olaf J. Borkiewicz^c, Kamila M. Wiaderek^c, Ali Darwiche^d, Joshua M. Stratford^a, Karena W. Chapman^c, Peter J. Chupas^c, Laure Monconduit^d & Clare P. Grey^a

^aUniversity of Cambridge, UK, email: pka22@cam.ac.uk;

^bGonville and Caius College, Cambridge, UK; ^cArgonne National Laboratory, USA; ^dUniversité Montpellier, France.

Sodium-ion batteries have attracted attention in recent years because of the abundance of sodium compared to lithium, making them particularly attractive in applications such as large-scale grid storage where low cost and sustainability, rather than light weight is the key issue. Several materials have been suggested as cathodes but far fewer studies have been done on anode materials and, because of the reluctance of sodium to intercalate into graphite, the anode material of choice in commercial lithium-ion batteries, the anode represents a significant challenge to this technology. Materials which form alloys with sodium, particularly tin and antimony, have been suggested as anode materials; their ability to react with multiple sodiums per metal-atom give potential for high gravimetric capacities. However, relatively little is known about the reaction mechanism in the battery, primarily due to drastic reduction in crystallinity during (dis)charging conditions, but also because the structures formed on electrochemical cycling may not be alloys known to exist under ambient conditions [1].

In this study, we present a study of antimony as an anode in sodium-ion batteries, using in situ pair distribution function (PDF) analysis combined with ex situ solid-state nuclear magnetic resonance studies. PDF experiments were performed at 11-ID-B, APS, cycling against sodium metal [2]. Inclusion of diffuse scattering in analysis is able to circumvent some of the issues of crystallinity loss, and gain information about the local structure in all regions, independent of the presence of long-range order in the material. This approach has been used to probe local correlations in previously uncharacterised regions of the electrochemical profile and analyze phase progression over the full charge cycle. This analysis has been linked with ex situ ²³Na solid-state NMR experiments to

examine the local environment of the sodium; these show evidence of known Na_xSb phases but indicate additional metastable phases may be present at partial discharge.

[1] Ali Darwiche, Cyril Marino, Moulay T. Sougrati, Bernard Fraïsse, Lorenzo Stievano, and Laure Monconduit, *J. Am. Chem. Soc.*, 2012, 134 (51), 20805–20811 [2] Olaf J. Borkiewicz, Badri Shyam, Kamila M. Wiaderek, Charles Kurtz, Peter J. Chupas and Karena W. Chapman, *J. Appl. Cryst.*, 2012, 45, 1261–1269

Keywords: Pair distribution function analysis, electrochemistry

MS05_P36

(De)lithiation Process of a Promising Electrode Material - Vanadium Sulfide, studied using Pair Distribution Function Analysis, Solid State NMR and XANES

Sylvia Britto^a, Xiao Hua^a, Michal Leskes^a, Xiaodong Xu^b, Olaf Borkiewicz^c, Karena W. Chapman^c, Peter J. Chupas^c, Jaephil Cho^b & Clare P. Grey^a

^aDepartment of Chemistry, Lensfield Road, University of Cambridge, Cambridge CB2 1EW, United Kingdom

^bNano Energy Storage Materials Lab, Interdisciplinary School of Green Energy, Ulsan National Institute of Science and Technology, Korea
^cX-ray Science Division, Advanced Photon Source, Argonne National Laboratory, Illinois 60439, USA

The low theoretical capacities of the conventional LiCoO₂ cathode materials (120-150 mAh g⁻¹) [1] and graphite anodes (372 mAh g⁻¹) [2, 3] used in rechargeable Li ion batteries fuels an intense search for alternative electrode materials capable of higher electrical storage capacities. One way of achieving a larger specific capacity is to explore materials that are capable of undergoing a wider change in oxidation states thereby allowing for the accommodation of more than one Li ion per transition metal ion leading to higher capacities. We have found that VS₄, which is found as the mineral patronite [4], also described as V⁴⁺(S₂²⁻), has enormous potential as an electrode material in combination with graphite oxide, with preliminary electrochemical data indicating a remarkably high charge capacity close to 900 mAh/g. This material crystallizes in the monoclinic symmetry and is comprised of uncommon eight-coordinate V⁴⁺ ions coordinated to S₂²⁻ dimers which are linked together as linear chains with alternating bonding (2.8 Å) and non-bonding contacts (3.1 Å) between the vanadium centers. The products of discharge/charge are nano-sized and therefore difficult to characterize by conventional crystallographic methods. In-situ and Ex-

situ Pair Distribution Function analysis combined with Solid State NMR and XANES indicate that the VS_4 reacts reversibly and throws valuable insights on the nature of the intermediates formed during discharge/charge.

-
- [1] Winter, M., Besenhard, J. O., Spahr, M.E., Novak, P. *Adv. Mater.* 1998, 10, 725.
[2] Dahn, J. R., Zhang, T., Liu, Y. H., Xue, J. S. *Science* 1995, 270, 5236.
[3] Megahed, S., Scrosati, B. *J. Power Sources* 1994, 51, 79.
[4] Poizot, P., Laruelle, S., Grugeon, S., Dupont, L. Tarascon, J.-M. *Nature* 2000, 407, 496.

Keywords: Li-ion battery, Pair Distribution Function Analysis, conversion mechanism

MS05_P37

Ultradense Hydrogen Physisorption in the Porous Magnesium Borohydride

Yaroslav Filinchuk^a, Nikolay Tumanov^a, Voraksmy Ban^a, Hyunchul Oh^b, Michael Hirscher^b, Bo Richter^c, Torben R. Jensen^c, Matthew R. Hudson^d, Craig Brown^d, Gail N. Iles^e & Scott W. Jorgensen^f

^a Institute of Condensed Matter and Nanosciences, Université Catholique de Louvain, Place L. Pasteur 1, 1348 Louvain-la-Neuve, Belgium,

^b Max Planck Institute for intelligent systems, Heisenbergstrasse 3, D-70569 Stuttgart, Germany,

^c Center for Materials Crystallography, Interdisciplinary Nanoscience Center and Department of Chemistry, Aarhus University, Langelandsgade 140, 8000 Aarhus C, Denmark,

^d Center for Neutron Research, National Institute of Standards and Technology, Gaithersburg, MD 20899, USA,

^e Department of Crystallography, Helmholtz-Zentrum Berlin, 14109 Berlin, Germany,

^f Chemical and Environmental Sciences Lab General Motors R&D Center, 30500 Mount Rd, Warren, MI 48090, USA
e-mail: yaroslav.filinchuk@uclouvain.be

Recently the first porous hydride, $\gamma\text{-Mg}(\text{BH}_4)_2$, featuring so-called "borohydride framework" and capable to store reversibly guest species was discovered [1]. This example clearly shows that the covalently bound hydride anions, such as borohydride, can act as directional ligands, capable to form molecular and polynuclear complexes, as well as framework structures typically occurring in classical coordination chemistry. Various small molecules are reversibly absorbed in $\gamma\text{-Mg}(\text{BH}_4)_2$.

In this work we show that molecular hydrogen and nitrogen have different adsorption sites in $\gamma\text{-Mg}(\text{BH}_4)_2$, leading to different capacities on saturation and to different H_2 and N_2 BET areas. Only up to 0.66 N_2 molecules are adsorbed per Mg atom, but the saturation capacity is double (1.33 per Mg) for the smaller hydrogen molecule. Moreover, at higher pressures, the second hydride phase $\gamma\text{-Mg}(\text{BH}_4)_2 \cdot 2.33\text{H}_2$ forms with

unprecedented hydrogen content of ~22 weight %. The density of molecular hydrogen adsorbed into the pores (0.144 g/cm^3) is twice (!) higher than in liquid hydrogen (0.071 g/cm^3), having no analogues among other porous systems.

On the technical side, we will illustrate how *in-situ* diffraction at neutron and synchrotron sources allows to follow adsorption isobars, aiming for extraction of isosteric heats of adsorption directly from diffraction data, as well as for clarifying the microscopic mechanisms in terms of guest-host and guest-guest interactions. Using powder neutron diffraction data from freshly prepared $\gamma\text{-Mg}(\text{BD}_4)_2$ sample we reliably determined position and amount of adsorbed hydrogen that coincide with synchrotron powder diffraction data and BET experiments.

-
- [1] Filinchuk, Y. *et al.*, *Angew. Chem. Int. Ed. Engl.* 50, (2011) 11162.

Keywords: energy materials, hydrogen storage, metal borohydrides, in-situ diffraction, porous solids

MS05_P38

Decomposition of $\gamma\text{-Mg}(\text{BH}_4)_{2-x}$ composites, $X = \text{LiH, NaH, CaH}_2, \text{MgH}_2$

Elisabeth Grube^a, Steffen Riis Højbjerg Jensen^a & Torben René Jensen^a

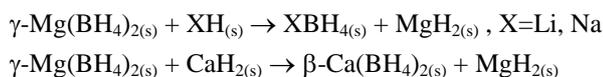
^aInterdisciplinary Nanoscience Centre and Department of Chemistry, Aarhus University DK-800 Aarhus, e-mail: trj@chem.au.dk

In order to implement hydrogen fuel vehicles in the future a compact, safe, efficient, and affordable way of storing hydrogen is needed. Metal borohydrides are considered suitable hydrogen storage materials as they have high gravimetric and volumetric hydrogen capacities. Recently Filinchuk *et al.* [1] discovered a new polymorph of magnesium borohydride, $\gamma\text{-Mg}(\text{BH}_4)_2$, which has a large permanent porosity and is the first borohydride capable of storing molecular hydrogen, thus making it very interesting for hydrogen storage. However, as most of the metal borohydrides the temperature-pressure conditions and the rate at which the hydrogen can be released is not appropriate for on-board hydrogen storage. One possible way of destabilising the borohydride and thus lowering the desorption temperature for hydrogen is by combining it with other compounds.

In order to examine how the presence of different metal hydrides influence the decomposition and hydrogen desorption compared to the pristine $\gamma\text{-Mg}(\text{BH}_4)_2$, we have investigated samples of $\gamma\text{-Mg}(\text{BH}_4)_{2-x}$,

X = MgH₂, LiH, NaH, or CaH₂ (2:1, 1:1, 1:2) with *in situ* synchrotron radiation powder X-ray diffraction (SR-PXD) in the temperature range RT to 300-500 °C. Also Thermogravimetric Analyses coupled with Mass Spectroscopy (TGA-DSC-MS) has been performed aiding to the understanding of the decomposition behavior of the samples.

Preliminary results show that the addition of metal hydrides has no positive effect on the temperature of hydrogen release. NaH and CaH₂ even have a negative effect increasing the temperature of hydrogen release with ~30 °C. However, results from the SR-PXD and TGA-MS experiments, indicate that the following cation substitution reactions are taking place during heating:



[1] Y. Filinchuk et al., *Angew. Chem. Int. Ed.* 50, 2011, 11162-11166.

Keywords: Hydrogen Storage, gamma Magnesium borohydride, *in situ* synchrotron radiation powder X-ray diffraction, cation substitution.

MS05_P39

Nanoconfinement of extremely low melting eutectic metal borohydrides: LiBH₄-KBH₄

Bjarne R. S. Hansen^a, Morten B. Ley^a & Torben R. Jensen^a

^aInterdisciplinary Nanoscience Centre and Department of Chemistry, Aarhus University DK-8000 Aarhus. E-mail: brsh@chem.au.dk

The eutectically melting composite of LiBH₄-KBH₄ has been determined to be 0.725 LiBH₄ - 0.275 KBH₄ and has a remarkably low melting point of $T = 105$ °C. This is the lowest reported melting point of any alkali and alkali-earth borohydride mixtures. This property makes it attractive to melt infiltrate LiBH₄-KBH₄ into a Resorcinol-formaldehyde-carbon aerogel (CA), in which other systems has shown improved hydrogen storage properties owing to thermodynamic and kinetic alterations.[1-2] The aerogels used here are either empty or pre-infiltrated with Mg particles. This is performed by solvent infiltrating magnesium dibutyl in heptane, Mg(Bu)₂, which is hydrogenated to MgH₂. The MgH₂ in the aerogel is heated under vacuum to form nanodispersed Mg particles. The aerogel samples are mixed in molar ratio 2(0.725 LiBH₄-0.275 KBH₄)-Mg or to fill 80 vol% of the empty aerogel. In bulk samples of LiBH₄-KBH₄ a small hydrogen release is observed after melting at $T = 105$ °C, however major hydrogen release is initiated at 400 °C (similar to pure LiBH₄).

The nanocon-fined samples show major hydrogen release already at 175 °C, hence a clear decrease in decomposition temperature of the eutectic mix is observed. Subsequent hydrogen cycles reveal improved cyclic stability in the nanoconfined samples, where hydrogen release initiates at 275 °C. In Figure 1 the improved hydrogen release and cyclic stability obtained by nanoconfinement is illustrated as the desorbed hydrogen (relative to the amount of hydride) shown for both the bulk and nanoconfined sample of the LiBH₄-KBH₄ eutectic system. Similar effects are observed in the bulk and nanoconfined samples with Mg particles.

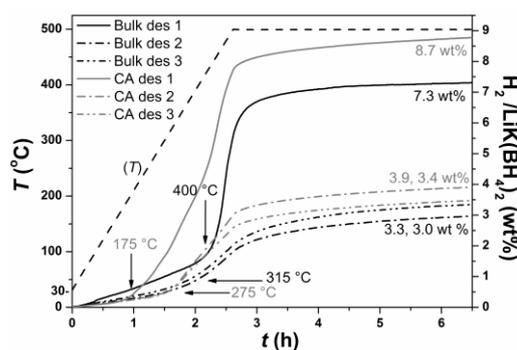


Figure 1. Sieverts desorption measurements of bulk LiBH₄-KBH₄ (black lines) and nanoconfined LiBH₄-KBH₄ (grey lines). The temperature profile is shown as a dashed line (T).

[1] T. K. Nielsen, U. Bösenberg, R. Gosalawit, M. Dornheim, Y. Cerenius, F. Besenbacher and T. R. Jensen, *ACS Nano*, 4 (2010) 3903-3908

[2] P. E. de Jongh, M. Allendorf, J. J. Vajo and C. Zlotea, *MRS Bull.*,38 (2013) 488-494

Keywords: Nanoconfinement, Hydrogen storage, Eutectically melting composite

MS05_P40

Ti-based Metal Hydrides for Concentrated Solar Thermal Application

Payam Javadian^a, Drew A. Sheppard^a, Torben R. Jensen^b & Craig Buckley^a

^aDepartment of Imaging and Applied Physics, Curtin University of Technology, GPO Box U 1987, Perth, Western Australia 6845, Australia,

^bCenter for Energy Materials, Interdisciplinary Nanoscience Center (iNANO), and Department of Chemistry, Aarhus University, DK-8000 Aarhus, Denmark. email: seydpaya@postgrad.curtin.edu.au

Solar energy is one of the most abundant renewable energy sources available on Earth; making efficient solar energy conversion into electricity or power a

highly focused research area. The issue with solar energy concentration is the limited energy supply available during daylight only. However by incorporation of a thermal energy storage system combined with a Concentrating Solar Thermal (CST) power plant, the energy supply will be available outside daylight hours. Metal hydrides are used in solar thermal energy storage systems medium for the thermochemical reactions taking place in the CST systems, due to their ability to absorb or desorb hydrogen simply by changing the applied pressure of the hydride bed. Concentrated solar energy is thermally stored in the hydride in a coupled system, with two different operating temperatures (high and low). By taking advantage of the endothermic hydrogen desorption (heat absorption) from the metal hydride, energy will be stored during sunlight hours. In periods of non-incident solar radiation hydrogen is stored (as low-temperature hydrogen) when the metal hydride re-absorb hydrogen in an exothermic process (heat release) [1-2].

Titanium is a transition metal that can form alloys with other metals e.g. aluminum, iron, molybdenum, to produce strong, lightweight, intermetallic compounds that are used for numerous purposes both in industry and on daily basis. In order to reduce the cost of titanium, while maintaining its abilities regarding absorption and desorption with hydrogen, titanium will be mixed with various metals. The thermodynamic properties of the following high temperature alloy systems will be investigated; Ti-Cu-H, Ti-Al-H, Ti-Fe-H, Ti-Mn-H and Ti-Zn-H. It is noted that the operating temperatures for these metal hydride are high (> 400 °C). These compounds will be characterized with regards to, chemical composition, thermal stability, thermodynamic properties, sorption kinetics and stability during hydrogen release and uptake cycling.

[1] Harries DN., Paskevicius M., Sheppard DA., Price TEC., Buckley CE, *IEEE*, 2012, 100, 539-49 [2] Fellet M., Buckley CE., Paskevicius M., Sheppard DA., *MRS Bulletin*, 2013, 38, 1012-13

Keywords: Concentrated solar energy, alloys, thermodynamics

MS05_P41

Nature's path to improved semiconductors

[Anders C. S. Jensen^a](#) & Henrik Birkedal^a

^aAarhus University, Denmark, hbirkedal@chem.au.dk

By controlling crystal formation and growth, nature has become an expert in creating specialized materials with extreme mechanical, magnetic and optical properties.

The natural materials like bone and mother of pearl have been studied extensively. However, there have been very few advances in making synthetic materials utilizing the concept from these materials.

Based on the strain effect in biogenic calcite Brif et al.[1] showed that amino acid could be incorporated into ZnO inducing strain and thereby changing the band gap of the semiconductor. Based on this work we will apply a co-block polymer of P(NIPAM-AAm)-b-PAA. In our system the PAA block interacts with the crystal structure inducing strain, while the P(NIPAM-AAm) block maintains its thermo-responsive properties. The result should be a semi-conducting, composite material with thermo-responsive properties.

[1] A. Brif, G. Ankonina, C. Drathen, B. Pokroy, *Advanced Materials*, 2013, 26, 477-481

Keywords: ZnO, Bio inspired, Material science

MS05_P42

Novel metal borohydride ammoniates

[Lars H. Jepsen^a](#), [Morten B. Ley^a](#), [Dorthe B. Ravnsbæk^a](#), [Yaroslav Filinchuk^b](#) & [Torben R. Jensen^a](#)

^aInterdisciplinary Nanoscience center and Department of chemistry, Aarhus University, Denmark

^bInstitute of Condensed Matter and Nanosciences, Université Catholique de Louvain, Belgium

Email: larsj@chem.au.dk

Metal borohydride ammoniates, $M(BH_4)_m \cdot nNH_3$, have potential as hydrogen storage materials owing to their low temperature for hydrogen release and high hydrogen content.

Here, we present synthesis of a range of novel solvent- and chloride-free metal borohydride ammoniates with tunable NH_3 content, i.e. tunable properties.

$Mn(BH_4)_2 \cdot nNH_3$ ($n = 1, 2, 3, 6$) and $Li_2Mn(BH_4)_4 \cdot 6NH_3$ have been prepared and the crystal structures for the four later are solved from synchrotron powder X-ray diffraction data. The coordination environment of Mn^{2+} changes from octahedral, to bipyramidal to tetrahedral for $Mn(BH_4)_2 \cdot 6NH_3$, $Mn(BH_4)_2 \cdot 3NH_3$ and $Mn(BH_4)_2 \cdot 2NH_3$, respectively. Hydrogen release via dihydrogen elimination from the interaction between partly positive hydrogen, $H^{\delta+}$, from NH_3 and partly negative hydrogen, $H^{\delta-}$, from BH_4^- take place for $Mn(BH_4)_2 \cdot nNH_3$ ($n = 1, 2$), while NH_3 is released for $n > 2$.

The rare earth metal borohydrides, $Re(BH_4)_2$ ($Re = Y, Dy, Gd$) are known to be isostructural [1]. However, while Y and Gd form a series of metal borohydride

ammoniates, i.e. $Y(BH_4)_3 \cdot nNH_3$ ($n = 7, 6, 5, 4$) and $Gd(BH_4)_3 \cdot nNH_3$ ($n = 6, 5, 4$), Dy only forms $Dy(BH_4)_3 \cdot 4NH_3$. Crystal structures have been solved for $Re(BH_4)_3 \cdot nNH_3$ ($n = 6, 5, 4$), while the crystal structure for $Y(BH_4)_3 \cdot 4NH_3$ is known [2].

A correlation is discovered between decomposition temperatures, T_{dec} , for metal borohydride ammoniates and the electronegativity, χ_p , of the metal. Destabilization is observed for metal borohydrides with low electronegativity, while metal borohydrides with high electronegativity are stabilized by NH_3 [3].

[1] T. Sato *et al.* Phys. Rev. B. 2008, 77, 104114 [2] F. Yuan *et al.*, J. Mater. Chem. 2011, 22, 1061 [3] L. H. Jepsen *et al.*, Mater Today, DOI: 10.1016/j.mattod.2014.02.015

Keywords: *In situ* X-ray powder diffraction, hydrogen storage, crystal structure determination

MS05_P43

Screening of catalytic additives to MgH_2 by p-T varied in situ synchrotron X-ray diffraction

Dmytro Korablov^{a,b}, Thomas K. Nielsen^a, Flemming Besenbacher^c & Torben R. Jensen^a

^aCenter for Materials Crystallography (CMC), Interdisciplinary Nanoscience Center (iNANO), Department of Chemistry, Aarhus University, Denmark, e-mail: korablov@chem.au.dk.

^bInstitute for Problems of Materials Science, NASU, Kyiv, Ukraine.

^cInterdisciplinary Nanoscience Center (iNANO) and Department of Physics and Astronomy, Aarhus University, Denmark.

Magnesium hydride is a promising material for hydrogen storage possessing high gravimetric and volumetric capacities (7.6 wt% H_2 and 109 g $H_2 L^{-1}$, respectively), cyclic reversibility and low costs. Major drawbacks of MgH_2 are high decomposition temperature (at least 300 °C) and the slow kinetics of hydrogen desorption and absorption. Among the best catalysts facilitating hydrogen release and uptake for MgH_2 are known oxides and halides of transition metals. Despite the fact that there are a lot of experimental evidences of the catalytic activity of chloride and oxides additives^{1,2} currently there is no clear picture and their mechanism of action^{3,4}. Composites of magnesium hydride mechano-chemically combined with selected transition metal hydrides, chlorides or oxides are investigated using *in-situ* synchrotron radiation powder X-ray diffraction (SR-PXD) studies. The aim is a more detailed investigation of kinetics and mechanism for hydrogen release and uptake for magnesium hydride. The fastest hydrogen desorption and absorption kinetics for MgH_2 was observed for a sample with 5 mol% V_2O_5 at 320 °C.

Additional activation of the system (2 cycles, vacuum/ $p(H_2)$ ~150 bar, 450 °C) leads to significant improvement of the kinetics even at lower temperatures, 270 °C. The observed prolific effect is achieved through the full reduction of vanadium oxides and formation of an efficient vanadium catalyst as nanoparticles and possibly interfacial effects in the $MgO/Mg/MgH_2/V$ system introduced during cycling hydrogen release and uptake in hydrogen/dynamic vacuum at 450 °C. Nanostructuring may improve the kinetics and reduce the apparent activation energy for hydrogen release. Thus, the enhancement of hydrogen release/uptake of the $MgH_2-V_2O_5$ system is possibly owing to '*in situ*' formation of vanadium nanoparticles by reduction of V_2O_5 .

[1] Varin RA, Zbronic L, Polanski M, Bystrzycki J., *Energies*. 2011, 4, 1-25 [2] Malka IE, Czujko T, Bystrzycki J., *Int J Hydrogen Energy*. 2010, 35, 1706-12 [3] Barkhordarian G, Klassen T, Bormann R., *J Phys Chem B*. 2006, 110, 11020-4 [4] Jin SA, Shim JH, Cho YW, Yi KW, *J Power Sources*. 2007, 172, 859-62

Keywords: hydrogen storage, magnesium hydride, vanadium pentoxide, ball milling, in situ synchrotron powder X-ray diffraction

MS05_P44

Magnesium nickel hydride synthesis from organometallic precursor and Ni nanoparticles

Paulina Kuziora^a & Marek Polanski^a

^aDepartment of Advanced Materials and Technologies, Military University of Technology, 2 Kaliskiego Str., 00-908 Warsaw, Poland; e-mail: mpolanski@wat.edu.pl

Application of novel method of synthesis of ternary magnesium based hydrides is presented on the example of Mg_2NiH_4 . Reaction between magnesium organometallic precursor and nickel nanoparticles under hydrogen pressure is shown. Heating the mixture under hydrogen pressure lead to formation of magnesium nickel hydride. X ray phase analysis of product of the synthesis revealed the presence of one of the polymorphs of magnesium nickel hydride after single step synthesis.

Keywords: hydrogen storage, magnesium nickel hydride, synthesis, XRD.

Alkali Metal Strontium Borohydrides

Kasper T. Møller^a, Morten B. Ley^a, Pascal Schouwink^b,
Radovan Černý^b & Torben R. Jensen^a

^aInterdisciplinary Nanoscience Centre and Department of Chemistry, Aarhus University DK-8000 Aarhus

^bLaboratory of Crystallography, Department of Condensed Matter Physics, University of Geneva, 1211 Geneva, Switzerland
E-mail of the corresponding author: kaspertm@chem.au.dk

Bimetallic borohydrides synthesized from alkali, alkali earth and transition metal borohydrides by mechanochemical treatment have received significant attention, because of their structural diversity and very high volumetric density of hydrogen [1-3]. Recently, new bimetallic compounds were found in the $\text{KBH}_4\text{-M}(\text{BH}_4)_2$ (M = Mg or Mn) system. Particularly, the novel perovskite structure of $\text{KMn}(\text{BH}_4)_3$ is interesting as it seem to occur with other compositions as well.

Recently, strontium borohydride, $\text{Sr}(\text{BH}_4)_2$, has been reported. $\text{Sr}(\text{BH}_4)_2$ decomposes at 350 °C into SrB_6 and SrH_2 [4]. Here, we study the formation and properties of new $\text{MSr}(\text{BH}_4)_3$ from $\text{MBH}_4\text{-Sr}(\text{BH}_4)_2$, M = Na, K, Rb and Cs mixtures using mechanochemical treatment i.e. ball milling.

We discovered new bimetallic compounds, $\text{KSr}(\text{BH}_4)_3$, $\text{RbSr}(\text{BH}_4)_3$ and $\text{CsSr}(\text{BH}_4)_3$, which have an orthorhombic perovskite crystal structure, similar to $\text{KMn}(\text{BH}_4)_3$. These new bimetallic compounds have been investigated by *in situ* synchrotron radiation X-ray powder diffraction (SR-PXD), thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC).

As reported in [4] the decomposition of $\text{Sr}(\text{BH}_4)_2$ is very difficult to analyze. Unfortunately, the new bimetallic compounds behaves similar to $\text{Sr}(\text{BH}_4)_2$ as the decomposition is very complex thus decomposition products have been determined *ex situ*. Additionally, reversibility has been tested using a Sieverts apparatus by conducting a desorption-absorption-desorption cycle. However, thermal stability of solid borohydride compounds owing to strong covalent and ionic bonding nature often provides high decomposition temperatures alongside slow kinetics and poor reversibility[5]. Indeed, this might be an advantage in respect to other applications e.g. ion conductors.

[1] L. H. Rude et al., *Phys. Status Solidi A*, 2011, 208, 1754 – 1773

[2] P. Schouwink et al., *J. Phys. Chem. C*, 2012, 116, 10829–10840

[3] D. B. Ravnsbæk et al., *Angew. Chem. Int. Ed.*, 2012, 51, 3582–3586

[4] D.B. Ravnsbæk et al. *Inorg. Chem.*, 2013, 52, 10877–10885.

[5] L. George, *Int. J. Hydrog. Energy*, 2010, 35, 5454–5470

Synthesis, structural characterization and thermoelectric proprieties of $\text{Sr}_x\text{Ba}_{1-x}\text{Nb}_2\text{O}_6$ (x = 0, 0.2-0.8, 1)

Giuditta Perversi^{a,b}, Espen Drath Bøjesen^b & Mogens Christensen^b

^aUniversity of Pavia, Italy, e-mail: giuditta.perversi01@ateneopv.it,

^bCenter for Materials Crystallography, Aarhus University, Aarhus, Denmark

Single crystalline and poly crystalline Strontium Barium Niobate (SBN), with various composition, has been widely studied due to its optoelectronic and ferroelectric proprieties.[1]

It has been recently reported that SBN have promising thermoelectric (TE) properties, due to a low thermal conductivity over a wide temperature range combined with a relatively high power factor.

Studies of single crystalline samples and highly textured polycrystalline samples strongly indicate that the electronic conductivity is highly anisotropic and it depends significantly on the oxygen stoichiometry. [2]

In this work, we present synthesis of the whole compositional range ($\text{Sr}_x\text{Ba}_{1-x}\text{Nb}_2\text{O}_6$ with x = 0, 0.2-0.8, 1) using different synthesis and sample preparation routes. These are: a traditional solid-state “shake and bake” synthesis; microwave assisted solid-state synthesis and direct synthesis using Spark Plasma Sintering (SPS).

The aim of the study is to elucidate how the change in reaction atmosphere, time and temperature relates to the microstructure, texture and structure of the synthesized polycrystalline SBN samples.

Powder X-ray diffraction (PXRD) combined with Rietveld refinement was used to extract information on texture, microstructure and crystal structure of the synthesized products.

Electron microscopy was utilized to support the results related to microstructure and texture.

Furthermore, characterization of the high temperature TE properties, resistivity, thermal conductivity, Seebeck Coefficient, Hall carrier concentration and mobility has been performed.

The trends in the measured TE properties were compared with trends in the structural, textural and microstructural parameters to establish a correlation between these and the sample preparation methods, and to point out eventual stability issues. The results from this study contributes to a better understanding how

polycrystalline SBN can be tailored towards TE applications.

[1] C. Nikasch, M. Göbbels *Journal of Crystal Growth* 269 (2004) 324–332 [2] Soonil Lee et al., *Appl. Phys. Lett.* 96, 031910 (2010)

Keywords: Thermoelectric materials, Solid State Synthesis, Microwave synthesis, Spark Plasma Sintering, Rietveld Refinement

MS05_P47

Toward the synthesis of earth alkaline hydrazinidoborane

Jean-Fabien Petit^a, Umit B. Demirci^a & Philippe Miele^a

^aIEM (Institut Européen des Membranes),
UMR 5635 (CNRS-ENSCM-UM2),
Université Montpellier 2

Place E. Bataillon, 34095, Montpellier (France)
e-mail: Jean-Fabien.Petit@iemm.univ-montp2.fr

Recently, hydrazine borane ($N_2H_4BH_3$) has been considered for solid-state chemical hydrogen storage. Remarkably, it presents four protic hydrogen ($H^{\delta+}$) in tandem with three hydridic hydrogen ($H^{\delta-}$). Therefore, it has high gravimetric (15.4 wt%) and volumetric ($146 \text{ g}\cdot\text{L}^{-1}$) hydrogen-storage capacities. In the field, the challenge has been to dehydrogenate hydrazine borane to a large extent under mild conditions (*i.e.* $< 85^\circ\text{C}$ and atmospheric pressure) while avoiding the formation of hazardous by-product(s), which is essential for mobile and on-board application. However, it failed: temperatures higher than 1000°C are required and unwanted gaseous/solid by-products form.

To destabilize hydrazine borane, a chemical strategy has been adopted. It implies mixing hydrazine borane with lithium hydride [1], which leads to the formation of a derivative, namely lithium hydrazinidoborane $LiN_2H_3BH_3$ (hydrogen content 11.6 wt%). Our group very recently showed that this compound has two phases [2]: a low temperature one, transforming to a high-temperature one at around 90°C . In parallel, another hydrazinidoborane has been prepared by mechano-synthesis. It is sodium hydrazinidoborane $NaN_2H_3BH_3$ (hydrogen content of 8.85 wt%) [3]. Then, attempt for elaborating the potassium analog has been unsuccessful because of the extremely high reactivity of the precursors ($KH + N_2H_4BH_3$). As a next step, we have envisaged synthesizing earth-alkaline (Mg, Ca) hydrazinidoboranes by mechano-synthesis, using CaH_2 and MgH_2 as precursors. The EPDIC 2014 will be thus a great opportunity to present our last achievements on

synthesis and characterization of these last derivatives of hydrazine borane.

[1] H. Wu, W. Zhou, F. E. Pinkerton, T. J. Udovic, T. Yildirim, J. J. Rush, *Energy Environ. Sci.* 2012, 5, 7531.

[2] R. Moury, U. B. Demirci, Y. Filinchuk, T. Ichikawa, K. Goshome, P. Miele, *chem Matter*, submitted

[3] R. Moury, U. B. Demirci, T. Ichikawa, Y. Filinchuk, R. Chiriac, A. van der Lee, P. Miele, *ChemSusChem*, 2013, 6, 667.

MS05_P48

Novel method for synthesis of ternary magnesium based hydrides

Marek Polanski^a

^aDepartment of Advanced Materials and Technologies, Military University of Technology, 2 Kaliskiego Str., 00-908 Warsaw, Poland; e-mail: mpolanski@wat.edu.pl

Novel method of synthesis of ternary magnesium based hydrides is presented. Reaction between magnesium organometallic precursor and transition metal under hydrogen pressure lead to formation of magnesium based transition metal hydrides. X-ray phase analysis was performed to prove the presence of desired products in synthesis products. Received powders were investigated by differential scanning calorimetry and temperature programmed desorption coupled with mass spectrometry. Obtained results show that method can be applied for desired materials synthesis, however to obtain high reaction yield some modifications to the process need to be applied.

Keywords: hydrogen storage, ternary hydride, synthesis, XRD, DSC.

MS05_P49

High pressure polymorph of $Mn(BH_4)_2$ with high volumetric hydrogen content

Elsa Roedern^a, Dorrit B. Nielsen^a & Torben R. Jensen^a

^aAarhus University, Department of Chemistry, Center for Materials Crystallography (CMC) and Interdisciplinary Nanoscience Center (iNANO) Denmark, e-mail: roedern@chem.au.dk

Hydrogen is a favorable energy carrier and storage medium for renewable energy. Due to its low volumetric energy density is it desirable to store hydrogen in the solid state, *i.e.* in metal hydrides.

Within transition metal hydrides, manganese borohydride, $\text{Mn}(\text{BH}_4)_2$, with a gravimetric hydrogen capacity of 9.53 wt% H_2 is an interesting candidate for hydrogen storage, owing to its high stability at room temperature, low decomposition temperature ($T_{\text{dec}} = 137$ °C) and the high abundance of manganese in the lithosphere [1,2]. We report a new high pressure polymorph of $\text{Mn}(\text{BH}_4)_2$ with tetragonal unit cell, that has an exceptional high volumetric hydrogen content of 142.0 g H_2/L , compared to 117.9 g H_2/L in trigonal $\text{Mn}(\text{BH}_4)_2$. The crystalline high pressure phase, denoted $\delta\text{-Mn}(\text{BH}_4)_2$, is isostructural to high pressure $\delta\text{-Mg}(\text{BH}_4)_2$ [3], corroborating the structural similarities of $\text{Mn}(\text{BH}_4)_2$ and $\text{Mg}(\text{BH}_4)_2$. The volume collapse of approximately 20 % was observed to occur during ball milling as well as under static pressure in a steel press. The transition pressure was determined by powder diffraction, using a diamond anvil cell. The temperature stability of the high pressure $\text{Mn}(\text{BH}_4)_2$ was studied by *in situ* synchrotron radiation X-ray powder diffraction at ambient pressure and in hydrogen atmosphere at elevated pressure ($p_{\text{H}_2} = 100$ bar).

- [1] Černý, R., *et al.*, J. Phys. Chem. C 113, (2009) 9003.
[2] Liu, R., *et al.*, J. Alloys Compd. 515, (2012) 32.
[3] Filinchuk, Y. *et al.*, Angew. Chem. Int. Ed. Engl. 50, (2011) 11162.

Keywords: energy materials, hydrogen storage materials, metal borohydrides, volumetric hydrogen content

MS05_P50

Alkali earth metal borohydride ammoniates

Ram Sarusie^a, Lars H. Jepsen^a, Magnus H. Sørby^b, Bjørn C. Hauback^b, Jørgen Skibsted^c & Torben R. Jensen^a

^aInterdisciplinary Nanoscience center and Department of chemistry, Aarhus University, Denmark

^bInstitute for Energy Technology, P.O. Box 40, Kjeller, Norway

^cInstrument centre for Solid-state NMR spectroscopy, Department of chemistry and Interdisciplinary Nanoscience, Aarhus University, Denmark
Email: ram89@inano.au.dk

Ammonia, NH_3 , is catalytically split to N_2 and H_2 and is a candidate for on-board hydrogen storage as a result of its high hydrogen content (17.3 wt%) and the ability to store 30 % more energy per volume than liquid hydrogen. However, due to the toxicity of NH_3 there are substantial safety issues that hamper widespread utilization. Ammonia reacts with metal borohydrides owing to formation of dihydrogen bonds and/or coordination to the metal producing metal borohydride ammoniates, $\text{M}(\text{NH}_3)_n(\text{BH}_4)_m$. This is a newer class of materials, which is interesting for both NH_3 and/or H_2 storage [1].

We have synthesized two solvent- and halide-free alkali earth metal borohydride ammoniates, $\text{Ca}(\text{NH}_3)_6(\text{BH}_4)_2$ and $\text{Sr}(\text{NH}_3)_2(\text{BH}_4)_2$. The crystal structure of $\text{Ca}(\text{NH}_3)_6(\text{BH}_4)_2$ is solved from synchrotron radiation powder X-ray diffraction (SR-PXD). It crystallizes in a cubic unit cell ($a = 10.986$ Å), and Ca is octahedrally coordinated by NH_3 , while the BH_4^- groups act as counter ions. The structure of $\text{Sr}(\text{NH}_3)_2(\text{BH}_4)_2$ is indexed in a tetragonal cell ($a = 6.54376$, $c = 8.54401$ Å) and is currently investigated by combined SR-PXD, powder neutron diffraction and ^{11}B and ^2D MAS NMR of the isotopic exchanged compound, $\text{Sr}(\text{ND}_3)_2(\text{BD}_4)_2$.

Both compounds, $\text{Ca}(\text{NH}_3)_6(\text{BH}_4)_2$ and $\text{Sr}(\text{NH}_3)_2(\text{BH}_4)_2$, release NH_3 upon thermal treatment observed by combined thermogravimetric analysis, mass spectrometry and *in situ* SR-PXD.

- [1] L. H. Jepsen *et al.*, Mater Today, DOI: 10.1016/j.mattod.2014.02.015

Keywords: *In situ* powder X-ray diffraction, hydrogen storage, powder neutron diffraction

MS05_P51

Size and Shape Control of $\text{SrFe}_{12}\text{O}_{19}$ Nanoparticles through Supercritical Synthesis

M. Saura-Múzquiz^a, C. Granados-Miralles^a, E. D. Bøjesen^a, J. Song^b, M. Dong^b & M. Christensen^a

^aCenter for Materials Crystallography, Department of Chemistry and iNANO, Aarhus University, Denmark

^bCenter for Nanotechnology (CDNA), Interdisciplinary Nanoscience Center (iNANO), Aarhus University, Denmark

Permanent magnets are key materials in the development of a sustainable future due to their many current and potential applications in the inter-conversion between kinetic energy and electricity. The high price and low availability of rare-earth metals used in strong permanent magnets nowadays, necessitates search for cheap rare-earth free materials with good magnetic properties.

A good candidate for this purpose is strontium hexaferrite, $\text{SrFe}_{12}\text{O}_{19}$. This material has a preferred axis of magnetization along the crystallographic c-axis, given by a high anisotropy constant. The uniaxial character provides a large theoretical maximum coercivity, making the compound a good candidate for hard magnet applications. However, bulk magnetic materials form multiple magnetic domains, inhibiting

full orientation of spins, and therefore reducing the energy product of the magnet. One way of avoiding this, is matching the particle size of magnetic compounds to the magnetic domain structure. By doing so, it is possible to reduce the energy lost in domain wall formation and thereby maximize the energy product.

Tailor-made nanoparticles of $\text{SrFe}_{12}\text{O}_{19}$, have been synthesized through supercritical hydrothermal synthesis in a continuous flow reactor. The study of synthetic parameters such as Sr:Fe ratio has been carried out, and tuning of particle size and morphology has successfully been accomplished. Results show formation of anisotropic nanoparticles of platelet-like shape, which are thin along the crystallographic c -axis, and large in the ab -plane. The aspect ratio of the nanoplatelets (ab/c) is variable, being highly dependent on particle size.

Structural characterization of nanoparticles has been performed by Rietveld refinement of powder X-ray diffraction data, Transmission Electron Microscopy (TEM) and Atomic Force Microscopy (AFM). Magnetic characterization has taken place with a Vibrating Sample Magnetometer (VSM).

Keywords: hydrothermal synthesis, permanent magnets, powder X-ray diffraction

MS05_P52

X-ray and neutron diffraction analysis of NASICON- type $\text{Li}_{1-x}\text{Al}_x\text{Ti}_{2-x}\text{P}_3\text{O}_{12}$

[Yoo Jung Sohn](#)^a, [Enkhtsetseg Dashjav](#)^a, [Thomas Kowoll](#)^a,
[Mirko Ziegner](#)^b & [Frank Tietz](#)^a

^aInstitute of Energy and Climate Research (IEK-1), Forschungszentrum Jülich GmbH, 52425 Jülich, Germany

^bInstitute of Energy and Climate Research (IEK-2), Forschungszentrum Jülich GmbH, 52425 Jülich, Germany E-mail: y.sohn@fz-juelich.de

Li-based NASICON (Na Super Ionic Conductor)-type material $\text{LiTi}_2(\text{PO}_4)_3$ belongs to the family of Li^+ ion conducting compounds. Its conductivity of Li^+ ions, its chemical stability and the possibility of modifying its properties, e. g. by substitution, render $\text{LiTi}_2(\text{PO}_4)_3$ an interesting material for solid electrolytes in Li^+ ion batteries [1-3]. Here we report the structural analysis of $\text{Li}_{1-x}\text{Al}_x\text{Ti}_{2-x}\text{P}_3\text{O}_{12}$, in which tetravalent Ti is substituted by trivalent Al. This material shows good ionic bulk conductivity of approximately 3 mS/cm [4]. Powder X-

ray and neutron diffraction analyses of $\text{Li}_{1-x}\text{Al}_x\text{Ti}_{2-x}\text{P}_3\text{O}_{12}$ were carried out at different temperatures. The measured samples contained minor amounts of LiTiOPO_4 , AlPO_4 , TiO_2 and SiO_2 as impurities. The powder diffraction data confirm that the main phase crystallizes in the NASICON-type material (space group: $R-3c$) and no structural changes were observed between 10 and 1123 K. The Rietveld analyses of the neutron diffraction data converged to the weighted R factor of 3.22%. The Al^{3+} ions randomly substitute the Ti^{4+} ions in the crystal structure of $\text{Li}_{1-x}\text{Al}_x\text{Ti}_{2-x}\text{P}_3\text{O}_{12}$, and therefore, excess Li^+ ions are charge compensating the aliovalent substitution. Besides a fully occupied Li position (6b), which can be easily identified, three possible positions for excess Li (18e, 36f, 6a) reveal significant nuclear density in the Fourier maps. However, a stable refinement is only achieved by placing excess Li on the 6a sites, yielding reasonable interatomic distances. Furthermore, the coordination polyhedron around the 6a site, a trigonal prism, is part of the ion conduction channels of the NASICON structure. The structure refinement, however, may be hampered by the presence of minority phases. Studies on single-phase material are in progress.

[1] H. Aono, E. Sugimoto, Y. Sadaoka, N. Imanaka, G-Y. Adachi, *J. Electrochem. Soc.*, 1993, 140, 1827. [2] X. H. Liu, T. Saito, T. Doi, S. Okada, J-I Yamaki, *J. Power Sources*, 2009, 189, 706. [3] C. Wessells, F. La Mantia, H. Deshazer, R. A Huggins, Y. Cui, *J. Electrochem. Soc.*, 2011, 158, A352. [4] Th. Kowoll, *Diploma thesis*, 2012, FZ Jülich, RWTH Aachen

Keywords: Li ionic conductor; NASICON; Crystal structure.

MS05_P53

Combinatorial ball milling - an effective tool for high throughput processing and synthesis of hydrogen storage materials

[Katarzyna Witek](#)^a & [Marek Polanski](#)^a

^aDepartment of Advanced Materials and Technologies, Military University of Technology, 2 Kaliskiego Str., 00-908 Warsaw, Poland; e-mail: mpolanski@wat.edu.pl

We present the novel approach to high throughput hydrogen storage materials synthesis. In current work, custom cylinder for planetary ball mill was designed and manufactured to enhance the mechanical milling/synthesis research experiments. Up to 16 samples can be ball milled during one experiment in inert gas atmosphere and samples can be taken independently. The milling efficiency was compared to the classical cylinder used in planetary ball mill by the

use of XRD phase analysis and DSC. XRD spectra of MgH₂ samples milled for different times and with different amount of catalyst addition are presented as well as DSC decomposition curves. Novel technique was found to be effective and very useful in high throughput synthesis of new materials.

Keywords: ball milling, combinatorial, high throughput, hydrogen storage, magnesium hydride

*Microsymposium MS06:
Progress in instrumentation*

*Chairs: Ron Smith, Rutherford Appleton Laboratory (UK)
Bob Cernik, SRS, Daresbury (UK)*

*Microsymposium: Monday 16 June 2014 Afternoon – iNANO building, 1593-012
Poster session: Monday 16 June 2014 – iNANO building, 1590-Foyer*

Keynote Lecturers:

MS06_K1

Integrating PXRD in Accelerated Materials Discovery

Samantha Y. Chong & Andrew I. Cooper

Department of Chemistry and Centre for Materials Discovery, University of Liverpool, Liverpool UK. e-mail: s.chong@liv.ac.uk

Technologies and instrumentation for high throughput (HT) synthesis and crystallization have been embraced by industry, particularly the pharmaceutical sector, and exploited to discover new materials, for example, in supramolecular chemistry [1].

Powder X-ray diffraction (PXRD) is routinely used to screen the products of HT synthetic processes, as the diffraction experiment requires limited sample preparation, is non-destructive and data collection is fast. Software has been developed for automated screening to identify samples of interest in terms of crystallinity and with reference to known materials [2].

Recent advances in computation have enabled the development of HT computational prediction and property screening [3]. In concert with HT preparative techniques, this raises the possibility of truly targeted synthesis of new functional materials.

With this ultimate aim, we are working to develop protocols for screening arrays of novel, primarily organic, functional materials obtained from HT methods. These include, for example, the synthesis of self-assembled systems from dynamic combinatorial libraries, and of crystal modifications – polymorphs, multicomponent crystals – of previously synthesized compounds. The workflows integrate several stages, including preparation of arrays of samples on robotic platforms, characterization by PXRD, and assessment of properties, such as porosity to specific gases. Consideration must be given to reducing sample transfers and processing, and optimization of instrumentation to achieve rapid throughput.

While its use in initial screening is accepted, the complexity of structure determination from PXRD still generally precludes this role in HT workflows. The potential of parallel characterization techniques and information from computational methods to supplement powder diffraction data may broaden its contribution to HT materials discovery. We will briefly discuss possible strategies to realize this application.

[1] Banerjee, R. *et al. Science* **2008**, *319*, 939. [2] Barr, G. *et al. J. Appl. Crystallogr.* **2009**, *42*, 965; Baumes, L. A. *et al. Chem. Eur. J.* **2009**, *15*, 4258; *HighScore Plus*, PANalytical B.V., Almelo, Netherlands; Lau, D. *et al. Comb. Chem. High T. Scr.* **2011**, *14*, 28.

[3] Hachmann, J. *et al. J Phys Chem Lett* **2011**, *2*, 2241; Wilmer, C. E. *et al. Nat. Chem.* **2012**, *4*, 83; Abbott, L. J. *et al. J Mater Chem A* **2013**, *1*, 11950.

Keywords: High throughput, molecular material, porous materials.

MS06_K2

In-Situ Neutron Diffraction Studies of Electrode Materials for Li-ion Batteries

Matteo Bianchini^{a,b,c,d}, Emmanuelle Suard^a, Laurence Croguennec^{c,d} & Christian Masquelier^{b,d}

^a Institut Laue-Langevin, 6 rue Jules Horowitz, F-38000 Grenoble, France

^b Laboratoire de Réactivité et de Chimie des Solides, CNRS-UMR#7314, Université de Picardie Jules Vernes, F-80039 Amiens Cedex 1, France

^c CNRS, Univ. Bordeaux, ICMCB, UPR 9048, F-33600 Pessac, France

^d RS2E, Réseau Français sur le Stockage Electrochimique de l'Energie, FR CNRS#3459, F-80039 Amiens Cedex 1, France

In-situ techniques proved to be exceptionally useful tools to understand electrode materials for Li-ion batteries. However *in-situ* neutron diffraction (ND) knew a slow development, due to the intrinsic difficulties it held. The new electrochemical cell we designed, manufactured with a completely neutron-transparent (Ti,Zr) alloy, allows to overcome many of these. The scheme of the cell is reported in ref (1). Besides, the use of deuterated electrolytes minimizes the incoherent background coming from the cell. This way we are able to combine, for the first time, good electrochemical properties and the ability to collect neutron diffraction patterns *operando*, with good statistics and no other Bragg peaks than those of the electrode material of interest. This allows detailed structural determinations of electrode materials by Rietveld refinement during operation. The cell was validated using well-known battery materials such as LiFePO₄ and Li_{1.1}Mn_{1.9}O₄. The electrochemical signatures of the two materials were verified even with more than 200 mg of active material. To test the quality of the ND patterns, we measured for both materials fully assembled *in-situ* cells on the D20 diffractometer. The Rietveld refinement technique was used to demonstrate the possibility of its use on *in-situ* ND patterns (1). A real *operando* experiment was also conducted, where the active material LiFePO₄ was charged at C/24; upon charge 24 neutron diffraction patterns were acquired and refined. Results of this analysis will be presented. After these tests, the cell is now ready to be used to study new challenging materials. As an example, we measured the charge *operando* of a series of spinel materials Li_{1+x}Mn_{2-x}O₄ (x=0, 0.05, 0.1). From the data we observed how the material evolution upon charge strongly depends on x,

varying from a series of two-phase reactions to a solid solution. Results from the refinement of these data will be presented.

[1] M. Bianchini, J. B. Leriche, J.-L. Laborier, L. Gendrin, E. Suard, L. Croguennec and C. Masquelier, Journal of The Electrochemical Society, 160 (2013), A2176.

Keywords: electrodes, in-situ, operando, neutron diffraction, lithium batteries.

Oral Presentations:

MS06_O1

Resolving an instrumental conundrum: Bragg-Brentano and linear detectors

Bernd Hinrichsen^a & Arnt Kern^b

^aBASF SE, Germany, e-mail:bernd.hinrichsen@basf.com
^bBruker AXS, Germany, arnt.kern@bruker-axs.de

A huge fraction of powder diffractometers sold every year are based on the parafocusing Bragg-Brentano geometry. It combines sample preparation ease with high intensities and good instrumental resolution. The introduction of linear detectors has improved the data quality immensely providing intensities that were impossible to attain little more than a decade ago. They do however have a fundamental flaw. When collecting data at very low angles, as is the case with many material families such as mesoporous materials, zeolithes, clays or MOFs the detectors have to be closed using slits and an electronically narrowed detector window to allow meaningful data to be collected. Selecting too wide an opening leads to starting angles well under 0° - a physically senseless undertaking. All due to well meant but overly simplistic data collection regimes. To boot a large detector opening at low angles ruins the otherwise excellent resolution of the BB geometry by smearing out reflections due to the extremely defocused detector edges.

A simple and elegant solution to these troubles has been very recently implemented in the latest linear detector to be introduced to the market. And overview of the geometry and functions governing the dynamic detector control ensuring high resolution, low background and physically meaningful data collection will be provided.

Keywords: instrumentation, Bragg-Brentano, linear detectors

MS06_O2

New Facility for Long Duration Experiments at Diamond

Claire A. Murray, Paul Adamson, Sarah Day, Stephen P. Thompson, Jonathan Potter & Chiu C. Tang

*Diamond Light Source, Harwell Science and Innovation Campus, Didcot, Oxfordshire OX11 0DE, United Kingdom
e-mail: claire.murray@diamond.ac.uk*

The high brightness beamline I11 at Diamond Light Source is a dedicated powder diffraction instrument which has been in user operation for a number of years. Equipped with multi-analysing crystals (MAC) and fast position-sensitive detectors, it is routinely used for high-resolution and time-resolved experiments [1-3]. Recently, the beamline has undergone an upgrade to add a new facility for long duration experiments (LDE). Now at an advanced installation stage, the endstation (2nd experimental hutch) will house the necessary hardware and equipment for multiple LDE studies. These experiments will be mounted on a large sample table equipped with adjustable linear drives to automatically and periodically move sample cells in and out of the beam. A Pixium area detector, driven by a motorised stage, will record diffraction patterns. LDE will be set up and left in place with programmed automated data collections. Sample environments such as electrochemical cyclers, incubators, heating stages, environmental chambers and high pressure gas cells will be accommodated for user operation.

To complement the existing I11 facilities, the LDE hutch will open up new opportunities for those experiments which require weeks to months of periodically monitoring “slow” changes, up to two years. It will be of particular benefit to certain research areas, such as batteries and fuel cells, where important information on the development of phases over time cannot be obtained via ex-situ methods. Other research areas that will similarly benefit include studies of crystallisation, gas storage, mineral evolution, seasonal effects, thermal and electrical cycling and corrosion science. With a versatile design and many automated features such as robotic sample changers, this upgraded beamline is expected to be used by many academic researchers from diverse scientific backgrounds as well as from the pharmaceutical, nanotechnology, petroleum, minerals, defence, and speciality chemical industries.

[1] S. P. Thompson, J. E. Parker, J. Potter, T. P. Hill, A. Birt, T. M. Cobb, F. Yuan, and C. C. Tang, *Review Sci. Inst.* 2009, **80**, 075107
[2] S.P. Thompson, J.E. Parker, J. Marchal, J. Potter, A. Birt, F. Yuan, R.D. Fearn, A.R. Lennie, S.R. Street and C.C. Tang, *J. Synchrotron Rad.* 2011, **18**, 637

[3] J.E. Parker, S.P. Thompson, T.M. Cobb, F. Yuan, J. Potter, A.R. Lennie, S. Alexander, C.J. Tighe, J.A. Darr, J.C. Cockcroft and C.C. Tang, *J. Applied Crystallog.* 2011, **44**, 102

Keywords: Synchrotron Instrumentation, Long Duration Studies

MS06_O3

Towards routine data collection from hydrogenous materials using powder neutron diffraction

Paul F. Henry^{a,b}

^aEuropean Spallation Source (ESS) AB, PO Box 176, 221 00 Lund, Sweden,
^bDepartment of Chemical and Biological Engineering, Chalmers University of Technology, 412 96 Gothenburg, Sweden,
e-mail: paul.henry@ess.se

Hydrogen (¹H) is an element that is ubiquitous in chemistry and materials science. Neutron diffraction is the preferred technique for studying ¹H-containing compounds, but is complicated by the high incoherent scattering cross section, which also varies with wavelength, a variation that is not well understood. [1-3] This is surprising as it is the largest contributing factor to the scattering properties used in single crystal and powder neutron diffraction experiments to calculate the optimal sample size for hydrogen containing compounds. Additionally, the tabulated data are given for fixed neutron velocity of 2200 m s⁻¹ (approximately 1.8 Å). The use and current limitations of certain current generation neutron diffraction instruments to probe ¹H materials has recently been described. [4-5]

Here, I present work to validate an empirical correction for the incoherent scattering cross section of ¹H as a function of incident neutron wavelength in the range 0.5 - 10 Å using continuous source, monochromatic wavelength measurements. The practical use of this is that a, potentially quantitative, correction for all neutron diffraction data, including time-of-flight (TOF) from pulsed sources, as a function of scattering angle and neutron path length will become possible. Additionally, I will present work on an instrument concept for a pulsed monochromatic powder diffractometer for the ESS, which will be built in Lund by the end of the current decade. This diffractometer will aim to specialise in the data collection and analysis of hydrogenous materials using a combination of diffraction and inelastic techniques.

Implementation of methodology that allows routine H position definition from easily synthesised material – i.e. non-isotopically enriched, and in polycrystalline or small single crystal ($\leq 50 \mu\text{m}$) form – for both TOF and monochromatic neutron instruments would be of widespread application.

[1] J.A.K. Howard, O. Johnson, A.J. Schultz, A.M. Stringer, *J. Appl. Crystallogr.* 1987, 20, 120-122. [2] T.F. Koetzle, R.K. McMullan, 1980, Research memo C-4, Brookhaven National Laboratory, Upton, New York, USA. [3] C.D. Frost, 1989, Ill Internal report, Institut Laue-Langevin, Grenoble, France. [4] M.T. Weller, P.F. Henry, V.P. Ting, C.C. Wilson. *Chem. Commun.* 2009, 2973-2989. [5] C.C. Wilson, P.F. Henry, M. Schmidtman, V.P. Ting, E. Williams, M.T. Weller, *Crystallography Reviews*. 2014, DOI:10.1080/0889311X.2014.886202.

Keywords: neutron powder diffraction, hydrogen compounds, incoherent scattering

different operation modes electronically. Traditionally such structural information has been collected in separated experiments such as powder diffraction (PD), wide angle diffraction scale, small angle diffraction and direct space imaging techniques (sub-micronic to millimeter scale). HEIMDAL can offer these options in at the same time, therefore for absolutely identical experimental conditions.

The top-loading geometry foreseen not only accepts auxiliary from the ESS pool (cryogenics, pressure cells, magnets) but also allows implementing bulky brought-in user equipment. It can be pretested off-line at the instrument, but already fully connected to the HEIMDAL electronics

Keywords: multiple length scale NPD

MS06_O4

HEIMDAL: A time-of-flight neutron powder diffractometer at ESS for in-situ/in-operandi materials science studies

Sonja L.Holm^a, M. Bertelsen^a, Anar Singh^b, Jürg Schefer^b, Kim Lefmann^a & [Mogens Christensen^c](#)

^aNanoscience Center, University of Copenhagen, Denmark,

^bLaboratory for Neutron Scattering, Paul Scherrer Institut, Villigen PSI, Switzerland,

^cDepartment of Chemistry & iNano, University of Aarhus, Denmark, Jurg.Schefer@psi.ch

Developing new materials is of paramount importance to combat future energy demands, and environmental damage. Improvements in material performances are reached for example by the incorporation of advanced ceramics and polymers into heterogeneous systems. Their performances usually depend on the interplay between properties defined by the atomic, nano/mesoscopic and microscopic structure. *In-situ* and *in-operandi* investigations will be in the focus of such investigations. The instrument HEIMDAL proposed for the European spallation neutron source ESS will offer here perfect prospects, as the instrumental resolution of this powder diffractometer can widely be adapted and take full advantage of the broad pulse of ESS (2.86ms) offering highest intensity, or using a fraction of the pulse for highest resolution. A thermal and a cold guides pointing to the same virtual source extend the spatial window of the instrument from an atomic scale ($0.3 \text{ \AA}^{-1} \leq Q \leq 50 \text{ \AA}^{-1}$) to a nano/meso scale, $0.002 \text{ \AA}^{-1} \leq Q \leq 0.1 \text{ \AA}^{-1}$ by adding a narrow-band SANS instrument behind. Our chopper system allows switching the

MS06_P54

A large-area CMOS detector for high energy synchrotron powder diffraction and total scattering experiments

[Paula M. Abdala](#)^a, [Henrik Mauroy](#)^b & [Wouter van Beek](#)^a

^aSwiss–Norwegian Beam Lines at ESRF, BP 220, Grenoble, 38043, France.

^bPhysics Department, Institute for Energy Technology, P.O. Box 40, Kjeller, N-2027, Norway

The use of area detectors in synchrotron beam lines has had a large impact on crystallographic structural studies. Particularly, great progress has been achieved in time-resolved X-ray scattering experiments under in-situ (industrially relevant) conditions and in total scattering experiments by the combination of high energy photons available at synchrotron beam lines together with large area detectors.

In this work, a large area detector based on Complementary Metal–Oxide–Semiconductor (CMOS) technology is evaluated for X-ray scattering experiments with high energy (20 to 50 keV) photons. Its performance for X-ray powder diffraction and pair distribution analysis (PDF) has been demonstrated [1].

Data were collected on several compounds with different crystallinity (microcrystalline Ni powder, nanocrystalline doped-CeO₂ and amorphous SiO₂) and analyzed with classical Rietveld or PDF refinements.

Comparison of the analysis of reference compounds with literature and high resolution data collected on the same beamline demonstrate that the presented detector is suitable for crystallographic and total scattering experiments. The capabilities of the detector system for time resolved experiments has been evaluated by following the $\beta/\gamma \rightarrow \alpha$ phase transition in AgI using 1 sec exposure times.

The main advantages of the evaluated detector are its: fast read-out speed, good sensitivity at high X-ray energies, small pixel size and relatively low cost.

[1] P.M. Abdala, H. Mauroy, W. van Beek, *Journal of Applied Crystallography*, 2014, 47, page 449.

Keywords: CMOS, area detector, X-ray powder diffraction, pair distribution function, synchrotron radiation, time resolved.

MS06_P55

The Incoatec Microfocus Source I μ S for XRD-applications

[Bernd Hasse](#)^a, [André Beerlink](#)^a, [Jörg Wiesmann](#)^a & [Carsten Michaelsen](#)^a

aIncoatec GmbH, Max-Planck-Str. 2, 21502 Geesthacht, hasse@incoatec.de

The Incoatec microfocus source I μ S is a low power air cooled X-ray source for diffractometry applications. It is available with Cr, Co, Cu, Mo, and Ag anodes. The source is equipped with a two dimensional beam shaping multilayer optics. Therefore, we can form either a highly collimated beam with a low divergence (below 0.5 mrad) or a focusing beam with higher divergence (up to 10 mrad) and very small focal spots (diameter below 100 μ m).

The I μ S can be integrated in all X-ray diffractometry systems including full integration to interlock circuits. Also upgrades of existing diffractometers are possible.

Equipped with a collimating optics the I μ S can be used for GISAXS, SAXS and X-ray reflectometry studies. When using focusing optics all those experiments can be carried out in transmission geometry, especially in powder diffraction applications. The Co and Cr sources are useful for material characterization, especially for measurements of residual stresses in iron containing samples. Florescence radiation will not be excited. With the Mo and Ag-I μ S highly absorbing and radiation-damage sensitive materials can be investigated. Consequently, these sources are often used for single crystal diffractometry in the chemical crystallography and become more and more interesting for investigations of soft matter samples.

In our presentation we will give an overview of representative experimental setups and results demonstrating the potential of our I μ S in XRD studies. These take advantage of the brilliance and outstanding beam quality of this low-maintenance microfocus source. It is shown how the I μ S can be used to achieve excellent results in both home-lab and synchrotron pre-characterization experiments, e.g. the investigation of in-situ thin film deposition in UHV chambers or the structure of oriented two-dimensional liquid crystalline samples.

Keywords: Microfocus X-ray source, Upgrades, material characterization

Can X-Ray Diffraction Computed Tomography be achieved on a generic laboratory diffractometer?

Olivier Leynaud^a, Pierre Bordet^a, Géraldine Castets^b, Sophie Cersoy^a, Émilie Chalmin^b, Jean-Louis Hodeau^a & Pauline Martinetto^a

^aNéel Institute, Université Grenoble Alpes, France

^bEdytem, Université de Savoie, France
olivier.leynaud@neel.cnrs.fr

Can X-Ray Diffraction Computed Tomography be achieved on a generic laboratory diffractometer? Far from us the idea of competing or even getting close to experiments conducted with synchrotron radiation, such as recently described and developed [1]. No, the idea is to know whether basic investigations can be roughly carried out in a laboratory either as self-standing results or more realistically as preliminary studies to support a later proposal to obtain synchrotron beamtime. The main issue is acquisition time; therefore, even if a one week experiment is acceptable in a laboratory environment, highly precise reconstructions are out of reach. However, some results [2] have demonstrated that with a larger beam size than usual synchrotron experiments (about 150µm), quite large steps (30-40µm), and with an adequately chosen sample, a medium resolution reconstruction can reveal sufficient detail levels. In order to test the feasibility with such conditions on a generic laboratory instrument, we've developed a stand that has been implemented on a Kappa-CCD goniometer equipped with an Incoatec microsource (Ag radiation) and an ApexII detector. The stand consists in two manual translation and two motorized stages (one translation and one rotation) capable of submicrometric movements. The full assembly can perfectly fit on a goniometer head support making its installation almost timeless. We will present the stand and the first data collected on that experiment showing the actual feasibility of the full assembly. Further developments are in progress in order to improve scripts and optimise acquisition time and/or data quality.

That work has been supported by the PEPS Naïade.

[1] M. Álvarez-Murga & al., *J. Appl. Cryst.*, 2012, 45, 1109 (and references therein), [2] L. Religieux, *Master Thesis, Université Joseph Fourier, Grenoble, France*, 2011

Keywords: XRD-CT, Instrument development

Diffraction beamline I711 at MAX IV Laboratory

Francisco J. Martínez-Casado^a, Olivier Balmes^a, Dörthe Haase^a & Diana Thomas^a

^aMAX IV Laboratory, Lund University, Sweden.
e-mail: Francisco.martinez@maxlab.lu.se

Beamline I711 is a crystallography beamline used for powder diffraction[1,2]. The beamline uses a 13-period, 1.8 T, multipole-wiggler to produce X-ray light. The beamline now works at a fixed wavelength of 0.99 Å (12.5 keV). The beamline has a single crystal monochromator which provides a high photon flux at the sample while sacrificing easy tunability and high energy resolution. The experimental setup is a 4-circle diffractometer with kappa geometry, capable of doing both single crystal and powder diffraction using an area CCD detector. This set up is perfect for powder diffraction in-situ experiments (gas cells, temperature, pressure, etc.), and it has been in use for more than 10 years.

In the past months, the detector arm has been fitted with an analyzer crystal, with the aim of offering high resolution powder diffraction in the near future. In the preliminary tests, Rietveld refinement was carried out on some standards, and a resolution of 0.015° has been achieved.

[1] Y. Cerenius, K. Ståhl, L.A. Svensson, T. Ursby, Å. Oskarsson, J. Albertsson and A. Liljas, *J. Synchrotron Rad.* 2000, 7, 203. [2] M. Knaapila, C. Svensson, J. Barauskas, M. Zackrisson, S.S. Nielsen, K.N. Toft, B. Vestergaard, L. Arleth, U. Olsson, J.S. Pedersen, Y. Cerenius, *J. Synchrotron Rad.* 2009, 16, 498.

Keywords: synchrotron, powder diffraction.

Redefining the Concept of Multipurpose Powder Diffractometers

Fabio Masiello^a, Marco Sommariva^a, Natalia Dadivanyan^a, Olga Narygina^a, Detlef Beckers^a, Gwilherm Nénert^a & Martijn Fransén^a

^aPANalytical B.V., Almelo, The Netherlands, fabio.masiello@panalytical.com

Modern in-house X-ray diffraction systems are becoming more and more multipurpose analysis platforms, meaning that the same system can allow the

user to perform many different types of measurements with easy reconfiguration of the instruments. A wide variety of X-ray powder diffraction (XRPD) and scattering techniques are possible to characterize key structural parameters:

- particle size, size distribution, specific surface area and particle shape of nanoparticles by Small-Angle X-ray Scattering (SAXS);
- crystallite size, structure and phase identification by XRPD;
- thermal behavior and stability by in-situ heating and cooling experiments (non-ambient XRPD).

So far the multiple applications needed for the characterization of complex materials such as nanoparticles have been performed by exchanging pre-aligned optics (fixed slits, mirrors, monochromators...) which provide the *optimal* performance for each experimental setup [1,2]. Recently a new approach has been developed, which combines most of the benefits of the previously mentioned setups in just one solution; from the excellent monochromatization which leads to smooth and featureless background and improved detection limits, to better low-angle performance coupled with high intensity and peak resolution.

In this contribution we will give an overview of the range of applications which are possible with the new powder diffraction setup by investigating nanoparticle case studies.

[1] M. Sommariva, Solid State Phenomena 2013, 203-204, 17-20.
[2] M. Sommariva, M. Gateshki, J.-A. Gertenbach, J. Bolze, U. König, B.S. Vasile, V.-A. Surdu, Powder Diffraction 2014, submitted.

Keywords: Bragg-Brentano, powder, SAXS, multipurpose diffractometer, non-ambient

MS06_P59

A Versatile Diffractometer with a Double-Crystal Monochromator

[Pavol Mikula^a](#) & [Miroslav Vrána^a](#)

^aNuclear Physics Institute, Rez, Czech Republic
e-mail: mikula@ujf.cas.cz

Following our previous investigations [1], properties of a special neutron double-crystal monochromator employing bent perfect crystals of Si in (1,-1) and (n,-m) settings are presented. The first monochromator was the bent Si(111) crystal (4 mm thickness) and the second one was in the form of the sandwich consisting of two

bent Si(111) and Si(220) slabs (2 mm and 1.3 mm thickness, respectively). It has been found that by a simple exchange of diffraction conditions of the second monochromator one can use either Si(111) + Si(111) bent crystals in (1,-1) setting providing good luminosity and worse diffractometer resolution or Si(111)+Si(220) bent crystals in quasi-dispersive (n,-m) setting providing very good diffractometer resolution and correspondingly worse luminosity. It has been found that besides an excellent focusing and reflectivity properties of the quasi-dispersive double bent-crystal settings, the obtained monochromatic neutron current is sufficiently high for diffraction experiments even at the medium power research reactor. Such monochromator systems can at least be successfully exploited in diffractometers dedicated to residual strain/stress measurements when permitting strain/stress scanning (e.g. in the vicinity of welds) with good luminosity and worse resolution performance or microstrain studies (e.g. microstrain behaviour in samples under the external load) with the other high resolution performance. Furthermore, in the case of different lattice spacings of crystals in the (n,-m) setting, the double diffraction provides a monochromatic beam for high resolution in both $\Delta(2\theta)$ (2θ is the scattering angle) as well as $\Delta\lambda/\lambda$.

[1] P. Mikula, M. Vrána, J. Šaroun, V. Em, B.S. Seong, W. Woo, *Journal of Physics: Conference Series*. (2012), Vol. 340, 012014.
Doi:10.1088/1742-6596/340/1/012014

Keywords: neutron diffraction, monochromator

MS06_P60

Powder Diffraction with a Scanning 2D-area Detector Using Synchrotron Radiation: First Test

[Dmitry Molodenskiy^a](#), [Andrei Gogin^a](#) & [Sergei Sulyanov^b](#)

^aKurchatov Centre, Russia, e-mail: d.s.molodenskiy@yandex.ru,
^bInst. of Crystallography, RAS, Russia, sul942@yandex.ru

First test experimental powder diffraction data for LaB₆ NIST standard are obtained on the synchrotron radiation (SR) beamline installed in Moscow SR Centre on the source from a 19-pole wiggler. A standard optical scheme with two horizontal mirrors and a sagittal focusing monochromator is used. The goniometer provides the rotation of the CCD 1024x1024 area detector in the vertical plane to register maximum diffraction angles about $2\theta = 160^\circ$. The angular resolution is varied by choosing the sample-to-detector distance up to 1 m. A series of reference 2D-area

diffraction patterns from the powder standard inserted into 200 μm glass capillary was registered at different detector rotation angles. The angular accuracy of the 2θ -axis detector rotation in automatic regime was calculated by powder peak fitting and equaled $\Delta 2\theta = 0.001^\circ$. The whole $I(2\theta)$ dependence can be obtained by sewing the dependences calculated from 2D-area patterns registered at different detector rotation angles [1].

[1] S. Sulyanov, H. Boysen, C. Paulmann, E. Sulyanova, A. Rusakov, *Z. Krist. Proc.* 2011, 1, 175-180.

Keywords: powder diffraction, 2D-area (two dimensional) detector, SR

MS06_P61

Study of X-ray mirror optics and applications

[Takeshi Osakabe](#)^a, [Tetsuya Ozawa](#)^a, [Licai Jiang](#)^b & [Kazuhiko Omote](#)^a

^a*Rigaku Corporation, 3-9-12, Matsubara-Cho, Akishima-shi, Tokyo 196-8666, Japan*

^b*Rigaku Innovative Technologies Inc., 1900 Taylor Road, Auburn Hills, Michigan 48326, USA
e-mail: osakabe@rigaku.co.jp*

Optical configuration is one of the most important elements in x-ray diffractometry. Various optical systems are available for different types of measurement.

The para-focusing method is the most commonly used, since it provides high resolution and high intensity and is easy to use. On the other hand, the para-focusing method has some drawbacks, optical systems using the multilayer mirror are used for the following examples: thin-film samples requiring low-angle incidence, samples with strong preferred orientation, samples that cannot be pulverized or molded, profile analyses such as the Rietveld method and Pawley method, precision measurements of diffraction peak positions and widths, and measurements in special environments (temperature/atmosphere adjustment, etc.).

A multilayer mirror is an artificial lattice of alternating film layers of heavy elements and light elements. By altering the shape of the mirror and the thickness of the deposited layers, it is possible to convert divergent X-rays into parallel (less divergent) X-rays or convergent X-rays through the diffraction process. Parallel beam measurements have applications in powder diffraction, general asymmetric diffraction measurements, and in conjunction with high resolution crystal optics.

The ellipsoidal multilayer mirror is designed that one focus of the ellipsoid is placed at the focus of the X-ray source and the other focus of the ellipsoid falls on the detector plane. When measuring capillary samples in the transmission geometry, the measurement can be performed very efficiently if a 1D detector is used in combination.

We will show the new combination of the multilayer mirrors and applications.

Keywords: X-rays collimation, multilayer mirror, parallel beam, convergent beam

MS06_P62

GIXRD using the in situ reaction furnace at MCX

[Jasper Plaisier](#)^a, [Mahmoud Abdellatif](#)^a & [Andrea Lausi](#)^a

aElettra – Sincrotrone Trieste, Italy, e-mail: jasper.plaisier@elettra.eu

The Materials Characterisation by X-ray diffraction (MCX) beamline allows to perform a wide range of non-single crystal diffraction experiments: grazing angle diffraction and reflectivity, residual stress and texture analysis, phase identification and structural studies and kinetic studies. For the latter an in situ reaction furnace is installed that has been designed for diffraction experiments of powder samples in capillaries under a controlled atmosphere at high temperatures. An in house developed double capillary holder allows flowthrough of gases.

Recently, in order to extend the possibilities for the use of the furnace, it has been equipped with a new sample holder and goniometer. With the new set up it is possible to perform grazing incidence diffraction studies with temperatures up to 1373K. The furnace has a translating curved image-plate detector that allows real time measurements of diffraction patterns up to 130° 2-theta.

The new setup has been used in the study of the growth of ZnSe nanowires at low temperature. The nanowires were grown by molecular beam epitaxy, obtained by lowering the growth temperature down to 300 $^\circ\text{C}$. The low-temperature growth method has been developed using Si(111) and GaAs(111)B substrates. The process has been followed using in situ real time diffraction at the beamline MCX.

Keywords: GIXRD, furnace, synchrotron

MS06_P63

High(er) accuracy in structure analysis using MYTHEN detector

Dubravka Šišak Jung^{a,b} & Christoph Hörmann^a

^aDECTRIS Ltd, Switzerland

^bLaboratory for crystallography, ETH Zurich, Switzerland
e-mail: dubravka.sisak@dectris.com

Throughout 100 years of crystallography, the experimental setup remained deceptively simple and unchanged. The most remarkable breakthrough was the construction of the first synchrotron facilities in 1970ies. Nowadays, brilliance of the third (and fourth) generation synchrotrons can meet the requirements of material researchers but exceed the capabilities of traditional X-ray detectors. Therefore, the next big achievement was the development of single-photon-counting detectors. In the field of X-ray powder diffraction (XRPD), this new technology resulted in large (scalable) MYTHEN detector, whose features opened up new possibilities in time-resolved and high resolution XRPD measurements.

With focus on MYTHEN, developed at Paul Scherrer Institute and commercialized through DECTRIS [1, 2], this presentation will cover two topics: (i) what is single-photon counting (ii) how does this technology enhance XRPD data accuracy? By answering the questions about photon collection, sensors and readout chip, the first part, (i), provides the guidelines how to optimize the detector for a certain type of measurement. The second part, (ii), addresses crystallographic problems that could be solved only owing to MYTHEN's features: noise-free data, extremely high dynamic range, and reduced experimental time. Several novel structures of organic compounds will be presented to illustrate the enhanced accuracy and level of sophistication in structure analysis [3, 4]. In particular, the quality of the data will be discussed in the context of disordered systems, co-crystal *vs.* salt, and tautomer disambiguation. Additionally, the possibility of Rietveld refinement without geometrical restraints, data accuracy compared to the single-crystal case, and treatment of radiation-sensitive compounds will be addressed.

Successful application of MYTHEN detectors in laboratory XRPD analysis will be shown in several examples: one novel crystal structure of an organic compound, one known crystal structure as well as industrial stress measurements [5]. As last, re-design of the system for the optimization of stress measurements will be introduced.

[1] Schmitt, B et al. Nucl. Instr. Meth. Phys. Res. 2003, A501, 267-272

[2] Bergamaschi, A. et al. J. Synchrotron Rad. 2010, 17, 653-688

[3] Šišak, D. et al. *Angew. Chem. Int. Ed.* 2010, 49(26), 4503-4505

[4] Šišak Jung, D. PhD thesis. 2013, ETH Zurich

[5] Šišak Jung, D., Hörmann, Ch., Suominen, L., Parantainen, J. *Adv. Mat. Res.* 2014, in review

Keywords: detector, single-photon counting, MYTHEN, data accuracy

MS06_P64

A Simple Approach to Determine the Linear (σ - π) Polarization at SR Stations with 2D-area Detector

Sergei Sulyanov^a, Pavel Dorovatovskii^b & Hans Boysen^c

^aInstitute of Crystallography, RAS, Russia, e-mail: sul942@yandex.ru,

^bKurchatov Centre, Russia, e-mail: paulgemini@gmail.com,

^cLudwig-Maximilians-Universität, München, Germany, e-mail: boysen@lmu.de

Modern synchrotron radiation (SR) instrumentation including two-dimensional (2D) area detectors and special software for data treatment allow one to measure the scattered intensity with an accuracy of about 1%. Spatial polarization and absorption corrections are important steps during data reduction of 2D powder patterns. This is especially crucial for large diffraction angles necessary for up-to-date experimental data sets as required *e.g.* for electron density determination. A good knowledge of the linear polarization coefficient is mandatory for this purpose. A simple procedure for the measurement of the degree of linear polarization is described. The diffraction pattern from a glass plate set perpendicular to the incident beam is registered using a two-dimensional area detector. The intensity variation along the azimuth angle ρ at a constant diffraction angle is fitted to the theoretical $\cos^2\rho$ dependence. Results of measurements performed at a SR station with a CCD detector on the beam from the bending magnet are presented.

Keywords: linear polarization, 2D-area detector, SR

*Microsymposium MS07:
Diffraction line profile analysis, stress, strain and texture*

Chairs: Paolo Scardi, University of Trento (IT)

Daniel Loüer, Université de Rennes (FR)

Microsymposium: Monday 16 June 2014 Morning – Chemistry AUD I, 1514-213

Poster session: Monday 16 June 2014 – Chemistry AUD VI, 1510-213

MS07_K1

Strain distributions and diffraction peak profiles from crystals with dislocations

[Vladimir Kaganer](#)^a & [Karl Sabelfeld](#)^b

^aPaul-Drude-Institut für Festkörperelektronik, Hausvogteiplatz 5–7, 10117 Berlin, Germany, e-mail: kaganer@pdi-berlin.de

^bInstitute of Computational Mathematics and Mathematical Geophysics, Russian Academy of Sciences, Lavrentiev Prosp. 6, 630090 Novosibirsk, Russia

We have performed Monte Carlo simulations for different models of distributions of straight dislocations and found that the diffraction profiles and the strain probability distributions are very close to each other. In other words, the Stokes-Wilson approximation has a broad applicability range. Numerical calculation of the strain probability distribution is several orders of magnitude faster, since it does not involve an average of oscillating terms needed in a direct calculation of the peak profile. The strain probability distribution can be an effective tool for the diffraction profile calculation of more complicated dislocation distributions, for which the direct calculation is too computationally demanding.

Numerical and analytical calculations of the strain probability distributions of dislocations show that the distributions have a Gaussian shape only in the central part of small strain. This central part is due to contributions of many surrounding dislocations. The tails are due to large strain from few nearest dislocations and follow a power law. We demonstrate that, for straight dislocations, the Stokes-Wilson and the Krivoglaz-Wilkens approximations have the same applicability range and give the same result. The strain distribution statistics is very similar to statistics of gravitational forces due to a random distribution of stars and to velocity statistics of random vortices in turbulence.

We purposely modified the models of dislocation distributions to find the limits of the applicability of the Stokes-Wilson approximation. The approximation fails when the system possesses a long-range order evidenced by the coherent Bragg peak. In numerical calculations, presence of the long-range order can be traced by calculating the Debye-Waller factor. With the increasing reflection order, the Debye-Waller factor decreases, and the accuracy of the Stokes-Wilson approximation improves. Hence, this approximation can be applied to higher-order reflections even when it is not applicable for low reflection orders.

Keywords: line profile analysis, dislocations, Monte Carlo calculations

How far can powder diffraction quantify stacking disorder interaction ranges through full pattern analysis?

[Thomas C Hansen](#)^a, [Christian Sippel](#)^{a,b} & [Werner F Kuhs](#)^b

^aInstitut Laue-Langevin, 6 rue Jules Horowitz, BP 156, 38042 Grenoble Cedex, France, e-mail: hansen@ill.fr

^bGZG, Abt. Kristallographie, Universität Göttingen, Goldschmidtstr. 1, 37077 Göttingen, Germany, e-mail: wkuhs1@gwdg.de

Following some debate about the precise character of the stacking disorder of the so-called “cubic” ice phase Ic and stacking-faulted hexagonal ice Ih [1], we present here an overview of the effect of different stacking disorder ranges s from $s = 2$ to $s = 4$ after Jagodzinski [2–4] on the (neutron) powder diffraction patterns of, as an example, stacking-disordered ice I. We will fit in a systematic approach simulated data of s up to 4 with our model [5], applying different ranges s in the fitting, up to the underlying s of the fitted data. We will trace estimated standard deviations and correlations on the $2^{(s-2)}$ refined stacking probability parameters and the particle size in stacking direction for different circumstantial conditions of wavelength, resolution and coverage in 2θ of a constant wavelength diffractometer. In this way we can make a clear statement about the potential of distinguishing different models and quantifying the stacking disorder as a function of the diffractometer characteristics. The discussion can be easily extended to metallurgical problems and with some effort to other types of two-dimensional stacking disorder, e.g., in oxides.

[1] Kuhs WF, Sippel C, Falenty A, Hansen TC, *P Natl Acad Sci USA*. 2012, 109, 21259–21264

[2] Jagodzinski H, *Acta Crystallogr*. 1949, 2, 201–207

[3] Jagodzinski H, *Acta Crystallogr*. 1949, 2, 208–214

[4] Jagodzinski H, *Acta Crystallogr*. 1949, 2, 298–304.

[5] Hansen TC, Koza MM, Kuhs WF, *J Phys Condens Matter*. 2008, 20, 285104

Keywords: stacking faults, two-dimensional disorder, ice

Oral Presentations:

MS07_O1

Stacking fault energy determination using in situ X-ray diffraction

[David Rafaja](#)

Freiberg University of Technology, Freiberg, Germany
e-mail: rafaja@ww.tu-freiberg.de

In various materials, the stacking faults facilitate the phase transformations and hence influence the phase stability. Two examples of the relevant materials are metastable austenitic steels [1] and oversaturated cubic (Ti,Al)N solid solutions [2]. The propensity to form stacking faults depends mainly on the stacking fault energy.

Numerous methods for determination of the stacking fault energy were developed in the past. Most of them are based on a correlation between the stacking fault probability, the dislocation density and the stacking fault energy [3]. As the stacking fault energy is calculated from the density of both microstructure defects, i.e., stacking faults and dislocations [4], its accuracy is affected by the accuracy of these experimentally determined quantities in equal measure.

In this contribution, an in situ X-ray diffraction method will be presented, which determines the stacking fault energy in face centered cubic materials from a critical stress induced via sample bending. This method utilizes the results of Byun's consideration about the stress dependence of the partial dislocation separation [5], which evidenced (i) that the separation distance of the partial dislocations diverges, when the critical stress is reached, and (ii) that the critical stress is directly proportional to the stacking fault energy.

The central experimental method of the proposed approach is the in situ X-ray diffraction, which is primarily used for the measurement of the critical stress. In addition to the stress measurement, the in situ X-ray diffraction is employed to verify the diverging breadth of the stacking faults and to inspect their possible interactions with other microstructure defects. The capability of the proposed method was tested on highly alloyed austenitic steels containing chromium, manganese and nickel as the main alloying elements. The analogies and differences with respect to the classical Read & Schramm method [4] will be discussed.

- [1] S. Martin, C. Ullrich, D. Šimek, U. Martin and D. Rafaja, *J. Appl. Cryst.* (2011), 44, 779-787.
- [2] D. Rafaja, C. Wüstefeld, M. Dopita, M. Motylenko, C. Baecht, C. Michotte, M. Kathrein, *Surf. Coat. Technol.* (2014), doi: 10.1016/j.surfcoat.2014.01.039.
- [3] R.E. Smallman, K.H. Westmacott, *Phil. Mag.* (1957), 2, 669-683.
- [4] R.P. Read, R.E. Schramm, *J. Appl. Phys.* (1974), 45, 4705-4711.
- [5] T.S. Byun, *Acta Mat.* (2003), 51, 3063-3071.

Keywords: In situ X-ray diffraction, macroscopic stress, local lattice strain, stacking fault density, stacking fault energy

MS07_O2

Diffraction Profile Broadening Owing To Vacancies In LaNi₅: Simulations And In-Situ Neutron Diffraction

[T.A. Webb^a](#), [C.J. Webb^a](#) & [E.MacA. Gray^a](#)

^aGriffith University, Australia, e-mail: timothy.webb@griffithuni.edu.au

The effect dislocations have on a powder diffraction pattern has been well reported in the literature [1,2] and they are known to cause a broadening of peak profiles. However, work on the effect that vacancies have on diffraction patterns has been largely mathematical, with very little support from simulations or experimental data. In the conventional view [3], vacancies are defects of the first kind, which therefore do not cause a broadening of diffraction peak profiles, only a small shift in lattice parameter.

However, computer simulations were performed on a simulated particle with randomly distributed vacancies. A simulated strain field was used to represent the relaxation of nearby atoms around the vacancy. The diffraction profile was calculated using the Debye pairwise summation formula. These simulations showed that high vacancy densities do cause a broadening of the diffraction peaks.

An *in-situ* neutron diffraction experiment on the hydrogen storage alloy LaNi₅ was carried out using the High Resolution Powder diffractometer for Thermal neutrons (HRPT) at the Paul Scherrer Institut (PSI), Switzerland. Hydrogen cycled LaNi₅ is known to contain very high vacancy densities [4] and so was well suited to this experiment. Annealing LaNi₅ under vacuum *in-situ* showed that at temperatures as low as 200°C there was a decrease in diffraction peak breadth

(Figure 1). Since this is well below the annealing temperature for dislocations, this may be owing to annealing of vacancies. Therefore in this sample, vacancies appear to be behaving as defects of the second kind.

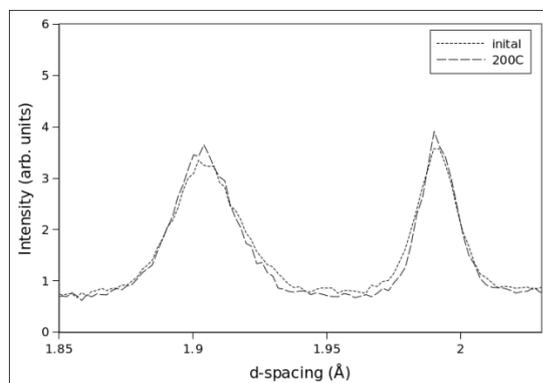


Figure 1: In situ diffraction profile of LaNi_5 before and after annealing at 200°C under vacuum

- [1] Kužel, R. & Klimanek, P., *Journal of Applied Crystallography*, 1988, 21, 363–368
 [2] Wu, E.; Gray, E. M. A. & Kisi, E. H., *Journal of Applied Crystallography*, 1998, 31, 356–362
 [3] Krivoglaz, M. & Glebov, O., "X-Ray and Neutron Diffraction in Nonideal Crystals", Springer London, 2011
 [4] Sakaki, K.; Araki, H. & Shirai, Y., *Materials Transactions*, 2002, 43, 1494–1497

Keywords: Vacancies, defects, peak profile

MS07_O3

Analysis of preferential orientation in zirconium samples deformed by uniaxial tension using neutron and X-ray diffraction

[Monika Kucerakova^a](#), [Stanislav Vratislav^a](#), [Ladislav Kalvoda^a](#) & [Zuzanka Trojanova^b](#)

^aCzech Technical University in Prague, Czech Republic
^bFaculty of Mathematics and Physics, Czech Republic
 e-mail: monika.kucerakova@fjfi.cvut.cz

Two series of zirconium samples were investigated by neutron and X-ray diffraction. First series of the samples was deformed on uniaxial tensile machine INSTRON 5882 at room temperature, whereas the second series was deformed at 300 centigrade. Both series were deformed from strain 0% to strain 30% (strain step was 5%). Preferred orientation parameters were determined by using pole figures and inverse pole figures.

The neutronographic texture measurements were performed on the KSN-2 neutron diffractometer located at the research reactor LVR-15 in the Nuclear Research Institute, plc. Rez, Czech Republic. The X-ray measurements were performed at theta/theta X'Pert PRO diffractometer with Cr X-ray tube.

Observed data were processed by software packages GSAS, TODF-N, ResMat and X'Pert Texture.

Planes (100) and (110) are oriented perpendicular to rolling direction. The position of the basal poles is tilted by 30° from the normal direction toward the transverse direction.

Planes (102) and (103) are oriented perpendicular to normal direction. Level of resulting texture increases with deformation.

[1] Kruzelova M., Vratislav S., Kalvoda L., Dlouha M., *Journal of Physics: Conference Series*. 2012, 340, 012095

Keywords: preferred orientation, zirconium, uniaxial strain, neutron diffraction, X-ray diffraction

MS07_O4

Design and management of a powder diffraction beamline for Line Profile Analysis: a realistic ray-tracing approach

[L. Rebuffi^{a,b}](#), [P. Scardi^a](#) & [M. Sanchez del Rio^c](#)

^aUniversità di Trento, Italy
^bElettra-Sincrotrone Trieste S.C.p.A., Italy, ^cESRF, France
 e-mail: luca.rebuffi@elettra.eu

Synchrotron Radiation (SR) is one of the main tools in the study of nanomaterials, in particular for powder diffraction, which fully exploits the high brilliance, energy selectivity and focusing conditions now routinely available at many beamlines. However, most facilities have been designed for studying conventional materials, whereas a modern approach to nanomaterials requires a complete control of the diffracted signal, and therefore of the optics and general set-up of the beamline [1]. This requirement is especially relevant when Line Profile Analysis (LPA) is pushed to the limits of large domain sizes, small deformations or low defects concentration, which is a driving force to use SR X-ray Diffraction.

We combine the SHADOW [2] simulation with the calculation of powder diffraction profile from standard materials, into a high-level workflow environment based on the Open Source ORANGE [3] software. Algorithms and software tools are developed to reproduce optical elements in a realistic form, so to

evaluate the effects of aberrations, with the final purpose of reconstructing and representing the Instrumental Profile Function (IPF) of the beamline, with the possibility of investigating the role of each separate element.

The results of this work, and the emerging paradigm, can be of interest to most beamlines for diffraction and other X-ray spectroscopies, as a powerful tool for the design of setups of existing as well as new beamlines.

-
- [1] F. Gozzo, A. Cervellino, N. Leoni, P. Scardi, A. Bergamaschi & B. Schmitt, "Instrumental profile of MYTHEN detector in Debye-Scherrer geometry", *Z. Kristallogr.* 225 (2012) 616
[2] M. Sanchez del Rio, N. Canestrari, F. Jiang and F. Cerrina, "SHADOW3: a new version of the synchrotron X-ray optics modelling package", *J. Synchrotron Rad.* (2011). 18, 708-716
<http://dx.doi.org/10.1107/S0909049511026306>
[3] <http://orange.birolab.si/>

Keywords: Instrumental Profile, Beamline, Design

Posters:

MS07_P65

Microstructural characteristics of corundum fillers

Joaquín Bastida^a, Pablo Pardo^b, Rafael Ibáñez^c, Marek A. Kojdecki^d, F. Javier De la Torre^e & Urquiola M^f

^aDepartamento de Geología, Universidad de Valencia, 46100 Burjasot (Valencia), Spain, e-mail: fer.garciatomas@gmail.com

^bDepartamento de Química Inorgánica, Universidad de Valencia, 46100 Burjasot (Valencia), Spain, e-mail: Pablo.Pardo@uv.es

^cInstituto de Ciencia de Materiales (ICMUV), Universidad de Valencia, 46980 Paterna, Valencia, Spain, e-mail: Rafael.Ibanez@uv.es

^dInstytut Matematyki i Kryptologii, Wojskowa Akademia Techniczna, 00-908 Warszawa, Poland, e-mail: m_kojdecki@poczta.onet.pl

^eDepartamento de Ingeniería Química, Universidad de Valencia, 46100 Burjasot (Valencia), Spain, e-mail: Javier.Torre@uv.es

^fDepartamento de Geología, Universidad de Valencia, 46100 Burjasot (Valencia), Spain, e-mail: M.Urquiola@uv.es

Corundum powders have a wide range of applications [1] but was considered unusual miscellaneous mineral fillers in plastics which improves electrical resistivity and thermal conductivity (mainly used in polyesters and epoxies) and reduces coefficient of thermal expansion and improves chemical inertness, hardness and abrasion resistance [2] but with increasing use as hard fillers for protective surfaces.

In the last years uses of hard alumina is increasing as filler in plastics, and thus it is interesting to compare microstructural features of corundum of different sources and their technological properties.

Corundum fillers of different ways of production (from: calcined alumina, hard calcined alumina, white fused alumina; ground, superground, jet milled, spray dried, and from other sources) are considered, and relevant properties are provided: particle size distribution (by laser diffraction system), mineralogical composition (by XRD powder diffraction), whiteness ($L^*a^*b^*$ CIELAB values under CIE 1931 observation standard) and apparent density.

Powder XRD crystallite size data by the Voigt function method [3] are provided as well as complementary descriptions of aggregation and microstructure by FESEM at different magnifications. The obtained values of 012* crystallite size were in the range 570-1940 Å. Different predominant particle shapes (blocky, platy, elongated, spheroidal) at different particle size fractions were observed as well as thickness normal to 012 flakes, with lower values of FESEM measured crystallite thickness [4] in the range 10-70 nm.

Different uses can be recommended considering that properties and microstructural features.

-
- [1] Baumgartner L.H (1990) pp 7-9, in LeRoy, D.H, editor, Alumina chemicals: science and technology handbook
[2] Walker B.M (1987), pp 232-242, in Katz H.S And Milewski J.V (Editors) Handbook of fillers for plastics.
[3] Langford, J.I., *Journal of Applied Crystallography*, 1978, 11, 10.
[4] Clausell, J.V., Bastida, J., Serrano, F.J., Pardo, P., and Huertas, F.J., *Applied Clay Science*, 2007, 37, 127.

Keywords: X ray diffraction, crystallite size, FESEM, MLS, kaolinite, smectite, reference clay, suspensions

MS07_P66

Analysis of local concentration profiles in mechanical alloyed TiN-AlN powder mixtures using X-Ray diffraction

David Chmelik^a & David Rafaja^a

^aTU Bergakademie Freiberg, Institute of materials science, Germany
e-mail: David.Chmelik@iwv.tu-freiberg.de

The aim of the proposed work was the investigation of the mechanical alloying of titanium nitride (TiN) with aluminium nitride (AlN) to create the face centered cubic metastable phase (Ti,Al)N. For this purpose, powder mixtures composed of 75 vol.% TiN and 25 vol.% AlN were milled for 3, 6, 9, 12, 15 and 30 hours with a constant ball to powder ratio (BPR) of 5:1 in a planetary ball mill. Another sample series was ball milled for 15 hours at the BPR of 10:1 and 20:1.

The phase composition and the microstructure of the produced powder mixtures were investigated by using powder X-ray diffraction (XRD) and scanning electron microscopy (SEM). The XRD measurements revealed an asymmetric line broadening of the TiN reflections to higher diffraction angles. The amount of the line asymmetry increased both with increasing milling time and with increasing BPR. We could show that this line asymmetry is caused by a concentration gradient of aluminum inside of the (Ti,Al)N particles. In order to determine the concentration gradient quantitatively, the measured XRD patterns were fitted by a convolution of two refineable physical XRD profiles and one measured instrumental XRD profile. One part of the physical profile was calculated from an error-function like concentration gradient, the second one from the line broadening due to the small crystallite size and microstrain. SEM gave an overview about the size and shape of the (Ti,Al)N particles.

The milling times up to 15 hours facilitated the fragmentation of the TiN crystallites and increased the amount of aluminum built into the host structure of

TiN. However, Al resided predominantly in the shell of the (Ti,Al)N particles. The core of the particles was enriched by Al after the milling time was extended and/or the BPR increased.

Keywords: XRD, titanium nitride, aluminum nitride, concentration profile, convolution, mechanical alloying

MS07_P67

On the Line Profile Analysis of pharmaceutical drugs

Pablo V. S. Lia Fook^a, Marica Broseghini^a, Cinira Fandaruff^b,
Cristy L. Azanza Ricardo^a, Luca Rebuffi^a, Helvécio Vinicius
Antunes Rocha^c, Silvia L. Cuffini^d & Paolo Scardi^a

^aUniversity of Trento, Italy

^bFederal University of Santa Catarina, Brazil

^cLab. Farmanguinhos – FIOCRUZ, Brazil

^dFederal University of São Paulo, Brazil

e-mail: pablo.viniciusdesousaliafook@unitn.it

Active Pharmaceutical Ingredients (APIs) used in long term therapies, like treatment of HIV, are frequently made of poorly soluble compounds. Therefore, reducing the amount of drug and improving the bioavailability are primary concerns of the pharmaceutical industry [1]. Standard micronization procedures provide little control on the final microstructure [2]. Even if the fine grinding to the nanoscale and presence of lattice defects might be the key to produce a new generation of more active and bioavailable drugs, almost no information can be found about alternative procedures for crystalline domain size reduction as well as for correlations between standard pharmaceutical parameters with microstructural properties. Powder diffraction can support R&D, well beyond the traditional structural studies, routinely used to assess crystallinity, phase composition and polymorphs, and exploit information from line profiles. Line Profile Analysis (LPA) on large unit cell organic phases is challenging, especially if the upper limit of measurable size must also be pushed up, above the traditional 200 nm, considered a practical limit in most cases [3]. In the present work we show potential advantages of using LPA, and how the information can explain the final performance of pharmaceutical compounds, mainly related to dissolution properties. Methodological issues are investigated, both concerning line profile modeling algorithms and experimental setups required for this specific application.

[1] Amidon, G.L.; Löbenberg, R., *European Journal of Pharmaceutics and Biopharmaceutics*, 2000, n.50, p.3-12

[2] Saleem, I. Y.; Smyth, H.D.C., *AAPS PharmSciTech*, 2010, Vol II, n. 4, p.1642-1649

Keywords: Active Pharmaceutical Ingredient, Line Profile Analysis, Organic Materials, crystalline domain Size.

MS07_P68

Coccolithophorids, Mussel Shells and Chalk - a comparison of the microstructure of biogenic calcite of different origin

[Simon Frølich](#)^a, [Sepideh Sadat Hakim](#)^b, [Henning Osholm Sørensen](#)^b, [Susan Stipp](#)^b & [Henrik Birkedal](#)^a

^a*iNANO & Dept. of Chemistry, Aarhus University, Denmark, e-mail: simonf@inano.au.dk, hbirkedal@chem.au.dk*

^b*Nano-Science Center, Department of Chemistry, University of Copenhagen, Denmark, e-mail: osholm@nano.ku.dk, stipp@nano.ku.dk*

In nature many organisms can control the polymorph, size, morphology and orientation of crystals in biomineralized tissues. Organic molecules are intimately involved in the nucleation and growth of biogenic crystals, directing specific structures to meet the needs of the parent organism. This close contact between the mineral and the organic material can lead to lattice distortions, which has previously been observed in biogenic shells [1,2]. Herein, *in-situ* heating and cooling was combined with synchrotron x-ray powder diffraction to show that the microstructure of biogenic calcite from chalk forming coccolithophorids differs from that of shells.

By performing two successive *in-situ* heating series of calcite, the contributions to the lattice strain by thermal expansion and occluded biomolecules can be separated. Data were collected at the high resolution diffractometer at ID31 of the ESRF, Grenoble. Rietveld refinements and multiple single peak analysis have been used to investigate the lattice strain response to the heating cycle. We examined both calcite from coccoliths freshly harvested from cultured coccolithophorids and calcite from shells.

The strain effects found in the coccoliths are significantly different from those observed in shell biogenic calcite. The strain effects found in the shells matched the previously reported behavior [2].

We suggest that the difference is caused by the high content of polysaccharides involved in the biomineralization of coccoliths, as opposed to the domination of proteins in other organisms. We recently

found that also non-shell aragonite behaves differently than shell aragonite [3], suggesting that the observed differences in microstructure reflect more general variations in the influence of occluded biomolecules on minerals.

[1] Pokroy, B., Quintana, J. P., Caspi, E. N., Berner, A., Zolotoyabko, E., *Nature Materials*. 2004, 3, 900-902 [2] Pokroy, B., Fitch, A., Zolotoyabko, E., *Advanced Materials*. 2006, 18, 2363-2368 [3] Leemreize, H., Eltzholtz, J. R., Birkedal H., *Eur. J. Miner.* 2014, accepted.

Keywords: Calcite, Biomineralization, Synchrotron Powder Diffraction, Lattice Strain)

MS07_P69

Comparative microstructural analysis (XRD and FESEM) and MLS behaviour of reference clay minerals.

[Fernando García Tomás](#)^a, [Pablo Pardo](#)^b, [Rafael Ibáñez](#)^c, [Marek A. Kojdecki](#)^d & [Joaquín Bastida](#)^a

^a*Departamento de Geología, Universidad de Valencia, 46100 Burjassot (Valencia), Spain, e-mail: fer.garciatomas@gmail.com*

^b*Departamento de Química Inorgánica, Universidad de Valencia, 46100 Burjassot (Valencia), Spain, e-mail: Pablo.Pardo@uv.es*

^c*Instituto de Ciencia de Materiales (ICMUV), Universidad de Valencia, 46980 Paterna, Valencia, Spain, e-mail: Rafael.Ibanez@uv.es*

^d*Instytut Matematyki i Kryptologii, Wojskowa Akademia Techniczna, 00-908 Warszawa, Poland, e-mail: m_kojdecki@poczta.onet.pl*

^e*Departamento de Geología, Universidad de Valencia, 46100 Burjassot (Valencia), Spain, e-mail: bastida@uv.es*

The present work deals with a set of very different clay minerals including three reference clays: kaolinite (KGa1) from Georgia kaolins, dioctahedral smectite (SWy-1, Wyoming Bentonite), dioctahedral calcium smectite (Saz-1, Cheto Bentonite) [1], and trioctahedral saponite (saponite Yunclillos supplied by Tolsa) and trioctahedral hectorite (Bentone HC, supplied by Elementis).

Granulometrical (laser diffraction system) and chemical data (ICP, INAA, ICP/MS and XRF techniques) of samples are provided. Microstructural analysis performed on X ray powder diffraction data by the Voigt function method [2] of <0.5µm fractions was carried out. Microstructure observation of aggregates and measurement of 001* crystallite thickness on FESEM images were performed by a previously established methodology [3]. Multiple scattered light analysis of diluted (2% volume fraction) aqueous suspensions was performed with a MLS analyzer to obtain averaged sedimentation rates.

The obtained values of Dv of 001* crystallite size by the Voigt function method were in the range 30-610 Å. FESEM measured crystallite thickness values were

found in the range 7.5-73.4 nm, exhibiting a fairly good correlation with Dv values.

The averaged sedimentation rates were in the range 0.30-8.20 $\mu\text{m}/\text{min}$, and their sequence was found to be in agreement with the increasing sequence of sizes estimated by the Voigt function method.

XRD and FESEM microstructural characteristics of the minerals allow the interpretation of the behaviour of the aqueous suspensions of the materials.

Thinner 001* crystallite size and edge-faces oriented structures of aggregates allow better stability of the suspension. Greater surfaces of 001* plate shaped crystallites and of their aggregates in 001 faces provide also lower velocity of sedimentation as measured by MLS as a result of parachute effect.

-
- [1] Chipera, S.J., Bish, D.L., *Clays and Clay Minerals*, 2011, 49, 398.
[2] Langford, J.I., *Journal of Applied Crystallography*, 1978, 11, 10.
[3] Clausell, J.V., Bastida, J., Serrano, F.J., Pardo, P., and Huertas, F.J., *Applied Clay Science*, 2007, 37, 127.

Keywords: X ray diffraction, crystallite size, FESEM, MLS, kaolinite, smectite, reference clay, suspensions

MS07_P70

Layered double hydroxides: structure, microstructure, and faulting from powder XRD

Robert Koch^a, Ferdinando Costantino^b, Marco Taddei^b & Matteo Leoni^a

^aUniversity of Trento, Trento, 38123, Italy
^bUniversity of Perugia, Perugia, 06123, Italy
e-mail: Robert.Koch@unitn.it, Matteo.Leoni@unitn.it

Layered Double Hydroxides (LDHs) are a rather versatile family of anionic clays that show unique promise in many fields of applied materials science. The possibility of substituting the cations and tailoring the anions in the interlayer leads to a variety of compounds with diverse and novel properties. Like their cationic counterparts, LDHs are characterized by the presence of stacking faults and interlayering of various polymorphs that introduce an extra complexity in the diffraction pattern.

While the literature on LDHs is quite rich, only qualitative microstructure parameters are generally extracted from powder diffraction. The analysis is in fact mostly limited to a pattern simulation [1] (aimed at reproducing the effects of stacking disorder) or to the analysis of the breadth of basal reflections [2]. Meaningful refinements which yield both quantitative

information on the structure, microstructure, and layer disorder are not common-place.

Here we show the application of a 2D-3D Rietveld-like approach embedding physically meaningful descriptions of the instrument and microstructure [3] and including a Markov-chain stacking algorithm [4] to model the powder diffraction data of CO_3^{2-} -LDHs. This approach allows for the refinement of the most probable faulting structure, as well as the size and shape of the crystalline domains in the sample.

-
- [1] G. S. Thomas, P. V. Kamath, *Chem. Sci.* 2006, 118, 127-133 [2] V. Drits, D. D. Eberl, J. Srodon, J., *Clays & Clay Minerals*, 1998, 46, 38-50. [3] P. Scardi, M. Leoni, *Acta Crystall. A* 2002, 58, 190-200 [4] M. J. Treacy, J. M. Newsam, M. W. Deem, *Proc. R. Soc. A*, 1991, 433, 499-520

Keywords: XRD, Stacking faults, domain size effects, Anionic clays, LDH

MS07_P71

Extraordinarily high density and thermal stability of nanotwins in Ni(W) films– An X-ray diffraction analysis

Silke J.B. Kurz^a, Andreas Leineweber^a & Eric J. Mittemeijer^{a,b}

^aMax Planck Institute for Intelligent Systems (formerly Max Planck Institute for Metals Research), Stuttgart, Germany
^bInstitute for Materials Science, University of Stuttgart, Germany
e-mail: s.kurz@is.mpg.de

The existence of planar faults generates diffuse intensity in the reciprocal space. If these planar faults are all equally oriented in the specimen frame of reference, the diffuse intensity forms pronounced streaks in reciprocal space. Such a specific arrangement enables a thorough analysis of planar-fault densities on the basis of X-ray measurements along the streaks in reciprocal space and evaluation by a statistical model describing transition probabilities for one to another type of stacking of close-packed layers as implemented in DIFFaX+ [1].

This kind of analysis has been applied to magnetron-sputtered Ni(W) thin films exhibiting a strong and sharp {111}-fiber texture and planar faults oriented parallel to the specimen surface. By means of the X-ray diffraction analysis, the degree of hexagonality of these initially fcc Ni(W) films has been identified in the as-deposited state. The degree of hexagonality was found to depend linearly on the W content of the films and reaches a degree of hexagonality of 65 % for the highest investigated W content. For W contents > 15 at.%, a two-phase nature of the film was observed, containing of fcc-like and hcp-like domains. This two-phase nature

necessitates the use of additional transition parameters in the statistical model. Twin- and stacking-fault densities were determined.

Further, investigations of Ni(W) films in a heat-treated state and during in-situ heating experiments were performed. The planar faults were found to be thermally stable if an explicitly hcp-like phase appears, i.e. for W contents > 18 at.%, which is in agreement with first-principles calculations. The described XRD analysis was validated by direct observation of stacking sequences by high-resolution transmission electron microscopy.

[1] M. Leoni, A.F. Gualtieri, N. Roveri, *J. Appl. Crystallogr.* 2004, 37, 166.

Keywords: X-ray diffraction, nanotwin analysis, thermal stability

MS07_P72

Towards understanding of double S phases

[Andreas Leineweber^a](#), [Matej Fonovic^a](#) & [Eric J. Mittemeijer^{a,b}](#)

^aMax Planck Institute for Intelligent systems (formerly Max Planck Institute for Metals Research), Stuttgart, Germany

^bInstitute for Materials Science of the University of Stuttgart, Germany

Austenitic stainless steel, i.e. fcc-type Fe-based alloys containing typically Ni and Cr, but also fcc-type Ni- or Co-based alloys containing e.g. Cr or Ti can take up unusually large, non-equilibrium amounts of interstitial nitrogen (introduced by various means) leading to an expansion of the lattice. The thus formed *expanded austenite* or *S-phase* is metastable against precipitation of alloying-element nitrides.

X-ray diffraction experiments, usually performed in symmetric reflection geometry of nitrided S-phase-forming alloy plates usually show pairs of Bragg peaks: for each *hkl* one reflection occurs due to the substrate and, at lower diffraction angles, one due to the S-phase at the surface of the substrate. Occasionally, apart from Bragg peaks due to the substrate, occurrence of *two separate* peaks has been reported [1] which may be attributed to *two distinct* S-phases with distinct lattice parameters.

Own studies on nitrided Ni-Ti alloys containing up to 5 at.% Ti subjected to gaseous nitriding also revealed the apparent presence of two distinct S phases of apparently distinctly different N contents. However, concentration-depth profiles determined by EPMA on cross sections of the nitrided alloy plates reveal a continuous decrease of the N content with increasing depth in the specimens,

hinting at presence of a single S-phase layer at the surface. It can be shown that these apparently contradicting observations can be reconciled by the occurrence of pronounced compressive stresses close to the surface of the S-phase layer and lower or even tensile stress levels in the depth of the S-phase layer, i.e. adjacent to the substrate. Generally, as reported previously [2], emergence of compressive stress is expected due to the incorporation of N, which is largely released by plastic deformation. It is here proposed that the remaining compressive stress is mainly determined by the concentration-dependent yield limit of the S phase which typically increases with increasing N content [3].

This view was obtained on the basis of tilting-angle dependent X-ray diffraction experiments showing a considerable shift to higher Bragg angles with increasing tilting angle of the low-angle peak due to the high-N content S phase component. This peak merges with the high-angle S phase peak at tilting angles where the diffraction vector is close to the strain-free direction.

[1] D.L. Williamson, J.A. Davis, P.J. Wilbur, *Surf. Coat. Techn.* 1998, 103-104, 178. [2] T.L. Christiansen, T.S. Hummelshoj, M.A.J. Somers, *Surf. Eng.* 2010, 26, 242 [3] M.O. Speidel: Ultrahigh strength austenitic stainless steels; Proceedings Stainless Steel World 2001 Conference, The Hague (NL).

Keywords: line-broadening analysis, macrostress

MS07_P73

X-ray diffraction line broadening from line defects in metal nanocrystals

[Alberto Leonardi^a](#) & [Paolo Scardi^a](#)

^aUniversity of Trento, Italy, e-mail: alby_jeo@yahoo.it; Paolo.Scardi@unitn.it

The effects of isolated line defects in Pd and Ir nanocrystals were studied by Molecular Dynamics simulations. Isolated edge and screw dislocations in bulk microstructures were stabilized after equilibration via Embedded Atom Method. A time-average of the atomic positions was computed, as to cancel the thermal effects out. Then, several nanoparticles of various shapes (i.e. sphere, cube, and cylinder) were carved out of the starting bulk microstructure.

The X-ray powder diffraction patterns of the nanocrystals were simulated using the Debye scattering equation [1]. Effects of statistical features were considered by averaging the patterns for nanoparticles with randomly positioned line defects. The simulated

patterns were subsequently analysed by traditional [2] and full pattern [3] Fourier methods.

The local atomic distortion field (microstrain) due to the defects was investigated according to the Krivoglaz-Wilkens theory [4]. A reasonable agreement was found, within Wilkens's assumption and approximations, between full pattern analysis and the true system features directly provided by the MD simulation. While it is interesting to see a direct and meaningful relation between the parameters of Krivoglaz-Wilkens's expressions and the dislocation-containing nanocrystals, serious limitations emerge in the underlying theory.

[1] P. Debye, *Anal. der Physik*, 1950, 351, 809 [2] B. E. Warren, et al., *J. Appl. Phys.*, 1950, 21, 595 [3] P. Scardi, et al., *Acta Cryst. A*, 2002, 58, 190 [4] M. Wilkens, *J. Appl. Cryst.*, 1979, 12, 119

Keywords: X-ray Powder Diffraction, Line Profile Analysis, Nanocrystalline materials, Dislocations, Molecular Dynamics simulation

MS07_P74

MStruct Extension for Extraction of Individual HKL-Profile Parameters Applied to Materials with Anisotropic Line Broadening

Zdeněk Matěj^a, Tereza Brunátová^a, Lenka Matějová^{b,c}, Václav Vales^{a,d}, Daniela Popelková^e & Radomír Kužel^a

^aCharles University in Prague

^bVŠB-Technical University of Ostrava

^cInstitute of Chemical Process Fundamentals of the ASCR, v. v. i.

^dJ. Heyrovsky Institute of Physical Chemistry of the ASCR, v. v. i.

^eInstitute of Macromolecular Chemistry of the ASCR, v. v. i., Czech Republic
e-mail: matej@karlov.mff.cuni.cz

Anisotropic line broadening is a very common effect especially for materials whose specific microstructure is related to their valuable properties. Analysis of profile parameters of individual diffraction lines is a very appropriate complementary method to the whole diffraction pattern fitting [1]. In the case of low symmetry or multiphase polycrystalline materials extraction of individual line profile parameters is complicated by peak overlap. With the presented extension of the MStruct [2] Rietveld code additional phenomenological line broadening components can be defined for selected *hkl* reflections and their parameters can be refined with an advantage of structural restrictions on line positions and intensities. Extracted profile parameters can be analysed by line profile methods (e.g. Williamson-Hall plot etc.). The method is

applied here to several types of materials. In the case of (a) nanocrystalline TiO₂ anatase samples [3] and (b) Na₂Ti₆O₁₃ titanate nanorods the method revealed a character and strength of possible anisotropic crystalline shape broadening effects. Contrary in (c) CeTi₂O₆ titanate [4] an anisotropic strain broadening was clearly the dominating effect. In all the cases the analysis of individual peaks profile widths was helpful both for building a reference model and for confirming its appropriateness for the whole profile fitting. It was useful for estimation of initial values of the model parameters as well.

[1] P. Scardi, M. Leoni, *J. Appl. Crystallogr.*, 2006, 39, 24
[2] Z. Matěj, R. Kužel, www.xray.cz/mstruct (Mar 28, 2014)
[3] Z. Matěj, L. Matějová, R. Kužel, *Pow. Diffr.*, 28, S161
[4] V. Valeš, L. Matějová, Z. Matěj, T. Brunátová, V. Holý, *J. Phys. Chem. Sol.* 2014, 75, 265.

Keywords: anisotropy, line profile, strain, nanocrystals, nanorods

MS07_P75

Mechanical Constraints and The Hydration Behaviour in the case of Na-Montmorillonite: Structural Analysis and Elastic Properties

Walid Oueslati^a

^aUR 05/13-01 : Physique des Matériaux Lamellaires et Nanomatériaux Hybrides (PMLNMH), Faculté des Sciences de Bizerte, Zarzouna 7021, Tunisia
^bTechnical and Vocational Training Corporation; College of Electronics & Communications, General studies department, TV street, P.O.Box 2816 Jeddah 21461, Kingdom Of Saudi Arabia
e-mail: walidoueslati@gmail.com

The experimental prediction of the mechanical properties of minerals remains difficult because of their small particle size (typically < 2 micrometers). This work aims at examining, the effect of an applied mechanical constraint on the hydration behaviour in the case of Na rich-montmorillonite and its relation with the elastic properties. The mechanical constraint is created, at the laboratory scale, by applying a monoaxial pressure for unstressed host material (i.e. Na rich montmorillonite). The structural analysis before and after stress is achieved using an XRD profile modeling approach. This investigation allowed us to determine several structural parameters related to the nature, abundance, size, position and organization of exchangeable cation and water molecule in the interlamellar space along the *c** axis. In order to evaluate the affected elastic properties, the GULP code have been used to study the structure and the

interlamellar organization. Indeed, the bulk modulus and elastic constants of montmorillonite have been calculated from first principles within density functional theory (DFT). The obtained Young's modulus for Namontmorillonite interlayer varies from 5 GPa to 16 GPa. According to the interlamellar space configuration the calculated elastic constant tensors indicate that the a direction is slightly more flexible than the b direction. The calculated elastic constant tensor along c is much lower than the constants calculated along a and b.

Keywords: Disordered system, Elastic properties, Gulp code, Hydration analysis

MS07_P76

Study of microstructure, hardness and residual stresses in FeB and Fe₂B ultra-hard layers

Zdenek Pala^a, Radek Musalek^b, Jiri Kyncl^a, Jiri Capek^a, Josef Strasky^c & Jaroslava Fojtikova^a

^aCzech Technical University in Prague, Czech Republic, zdenek.pala@fffi.cvut.cz, jiri.kyncl@fs.cvut.cz, capekjir@fffi.cvut.cz, jaroslava.fojtikova@fffi.cvut.cz

^bInstitute of plasma physics, Czech Republic, musalek@ipp.cas.cz, ^cCharles University in Prague, Czech Republic, josef.strasky@gmail.com

Boriding is a comparatively simple method of achieving ultra-hard surface on metals via thermo-chemical diffusion-based mechanism. For irons, the resulting surface hardness can be in the vicinity of 2000 HVN [1] and, in particular, two distinct crystalline phases, i.e. tetragonal Fe₂B, which has three polymorphs with space groups I-4/mcm or I-42m, and orthorhombic FeB (Pbnm) originate in the surface layer penetrated by boron ions. The spatial layout of the phases is usually such that the more brittle FeB is on the surface and the needles in deeper layers are grains of Fe₂B [2]. Even though differences in thermal expansion coefficients play an important role, macroscopic residual stresses or their spatial distribution in the altered layer are significant from the viewpoint of the new ultra-hard surface durability.

In our contribution, we have studied microstructure, hardness and spatial distributions of both phase composition and residual stresses in samples exhibiting either single phase Fe₂B or duplex Fe₂B-cum-FeB character. The indispensable knowledge of elastic constants used in stresses calculation from measured deformations by XRD were gained from the refined lattice parameters of both iron borides employing

density functional theory implemented in CASTEP [3] software by Material Studio

In all studied cases, Fe₂B has only minor occurrence of preferred orientation and the evaluated residual stresses have compressive character gradually decreasing from its maximal value on the very surface. However, the pronounced fibre 002 texture of FeB epitomized a hurdle for employment of standard algorithms in XRD stress analysis and called for unorthodox computations which took into account the volume fraction of material with texture and the texture quantitative characterization by pole figures and ODF.

[1] C.T. Zhou, J.D. Xing, B. Xiao, *Comp. Mat. Sci.*, 2009, 44, 1056-1064 [2] R. Prümmer, W. Pfeiffer, *J. Less-Common Met.*, 1986, 117, 411-414 [3] Information on <http://accelrys.com/products/materials-studio/index.html>

Keywords: boriding, surface hardening, iron borides, tooth-shaped microstructure, residual stresses.

MS07_P77

Stable and Metastable Ir—Os and Ir—Os—Ru Solid Solutions Prepared from Single-Source Precursors

Kirill V. Yusenko^a, Svetlana A. Martynova^b & Sergey A. Gromilov^{b,c}

^aUniversity of Oslo, Norway, e-mail: kirill.yusenko@smn.uio.no

^bNikolaev Institute of Inorganic Chemistry, Russia
^cNovosibirsk State University, Russia

Platinum group metals (PGM) play important role in catalysis, materials chemistry and technology. Their solid solutions can be prepared using melting or powder metallurgy, which requires high-temperatures and long reaction time. Nowadays, binary and ternary PGM solid solutions can be successfully prepared using soft conditions from technologically accessible single-source precursors [1, 2]. Here we report our recent systematic study of Ir—Os and Ir—Os—Ru solid solutions prepared from solid coordination compounds (NH₄)₂[Ir_xOs_{1-x}Cl₆] and [Ir_xRu_{1-x}(NH₃)₅Cl][Ir_yOs_{1-y}Cl₆] (x = y to fix Os/Ru ration as 1:1), correspondently, in the whole range of compositions. Thermal decomposition of precursors has been performed in hydrogen atmosphere at 600°C and results in the formation of *fcc* and *hcp* binary and ternary metallic solid solutions. Metallic phases were investigated using PXRD including detailed analysis of line-shape to characterize possible planar defects, size and stain

effects. Microscopy was applied for particles morphology characterization. Further annealing at 1000°C and ambient pressure was performed to understand stability of resulting phases under heating.

Thermal decomposition of $(\text{NH}_4)_2[\text{Ir}_x\text{Os}_{1-x}\text{Cl}_6]$ with $0.40 < x < 1.00$ results in the formation of *hcp*- $\text{Ir}_x\text{Os}_{1-x}$ single-phase solid solutions which are metastable in the region $0.40 < x < 0.60$ and transforms under heating (1000°C, 48 h, vacuum, ambient pressure) into two-phase mixtures. Compositions with $0.20 < x < 0.40$ are two phase and can be transformed into *fcc*- Ir — Os single-phase solid solutions. Metallic products with $0 < x < 0.20$ are *fcc*- $\text{Ir}_x\text{Os}_{1-x}$ single-phase. Composition dependence of atomic volume (V/Z , Å³) or whole range of *fcc* and *hcp* solid solutions can be fitted with the second order polynomial function with small positive deviation from linearity:

$$(V/Z) = 14.151(8) - 0.14(3) \cdot x_{\text{Os}} - 3(3) \cdot 10^{-2} \cdot x_{\text{Os}}^2.$$

Two ternary compositions appeared as a single phases: *hcp*- $\text{Ir}_{0.20}\text{Ru}_{0.40}\text{Os}_{0.40}$ with $a = 2.721(2)$, $c = 4.316(3)$ Å, $V/Z = 13.832(4)$ Å³ and *fcc*- $\text{Ir}_{0.80}\text{Ru}_{0.10}\text{Os}_{0.10}$ with $a = 3.832(2)$ Å, $V/Z = 14.067(4)$ Å³. Compositions in between are two-phase *fcc*+*hcp* mixtures.

[1] I.V. Korolkov, S.A. Gromilov, K.V. Yusenko, et al., *J. Structur. Chem.* 2005, 46, 1052 [2] K.V. Yusenko, E.A. Bykova, S.A. Gromilov, et al., *Phys. Rev. B* 2014, submitted

Keywords: iridium, osmium, alloys, phase diagrams

*Microsymposium MS08:
In situ, in operando studies*

*Chairs: Wojciech Paszkowicz, Institute of Physics (Warsaw, PL)
Claudia Weidenthaler, Max-Planck-Institut für
Kohlenforschung (DE)*

*Microsymposium: Tuesday 17 June 2014 Morning – iNANO building, 1593-012
Poster session: Tuesday 17 June 2014 – iNANO building, 1593-012*

Keynote Lecturers:

MS08_K1

Time and Space Resolved XRD Studies of Catalytic Reactors

[David Wragg](#)

*University of Oslo, Norway
e-mail: david.wragg@snn.uio.no*

Industrial catalytic reactors are often large and complex systems; however, due to the limitations of powder diffraction set-ups we often study them in situ in very limited model conditions, for example, using capillaries as models of much larger tube reactors and measuring at a single point with a focused beam. This can give excellent XRD data, but may not fully reflect the processes occurring in the larger scale reactor.

This presentation will cover attempts to study larger reactors using high energy X-rays to probe the sample with spatial as well as time resolution. This method reveals significant variations in the diffraction data from different areas of the reactor at different times in the reaction. The large volumes of data generated in these experiments can be treated efficiently using parametric Rietveld methods [1] to extract real structural information. Further processing can reveal very weak trends from the large data volumes obtained.

Using the methanol to olefin [2] and methanol to gasoline [3] processes as examples, I will demonstrate how the information obtained from time and space resolved diffraction experiments can be combined with spectral and modelling data to provide significant new insights into the processes occurring in larger scale reactors.

-
- [1] Stinton, G. W. & Evans, J. S. O. *J. Appl. Cryst.* 2007, 40, 87-95.
[2] Wragg, D. S., O'Brien, M. G., Bleken, F. L., Di Michiel, M., Olsbye, U., Fjellvåg, H., *Angew. Chem. Int. Ed. Engl.* 2012, 51, 7956-7959
[3] Wragg, D. S., Bleken, F. L., O'Brien, M. G., Di, M. M., Fjellvåg, H. & Olsbye, U. *Phys. Chem. Chem. Phys.* 2013, 15, 8662-8671.

Keywords: In Situ powder diffraction, Catalysis

MS08_K2

Combining in-situ X-ray techniques and related methods to obtain more information on dynamic systems

[Hermann Emerich](#)

*Swiss-Norwegian Beamlines SNBL at ESRF
ermano@esrf.fr*

Dynamically evolving processes like catalysis, material synthesis, diffusion and intercalation (batteries) are important issues in industry as well as in fundamental science.

In most of these systems physical properties like crystallinity, particle size, valency, lattice spacings or even the chemical composition of the studied material undergo huge changes during the reaction. Many experimentalists study their samples before and after the reaction, missing out on the intermediate steps which link both states. We, the Swiss-Norwegian Beamlines (SNBL) at the European Synchrotron (ESRF) propose an alternative approach by using different X-ray techniques, which are adapted to the variability of these systems. Being able to perform different x-ray measurements in a quasi-simultaneous way, we can follow these processes in real-time on the few seconds scale.

Additional non-x-ray based techniques like Raman, galvanometry and/or residual gas analysis (RGA) can be performed in parallel to enhance the information output even further. In this presentation I will show on the basis of a selection of real experiments how the multi-technique approach can be fine-tuned to cater for a wide range of dynamic systems.

Keywords: Powder diffraction, Exafs, PDF, in-situ, in-operando

Oral Presentations:

MS08_O1

Formation of γ -Fe₂O₃ in hydrothermal synthesis: *In situ* total scattering studies

Kirsten M. Ø. Jensen^{a,b}, Henrik L. Andersen^a, Christoffer Tyrsted^a, Espen D. Bøjesen^a, Nina Lock^a, Ann-Christin Dippel^c, Simon Billinge^{b,d}, Bo B. Iversen^a & Mogens Christensen^a

^aCenter for Materials Crystallography, Department of Chemistry and iNANO, Aarhus University, DK-8000 Aarhus C, Denmark

^bApplied Physics and Applied Mathematics, Columbia University, New York, New York 10027, United States

^cDeutsches Elektronen-Synchrotron DESY Photon Science, Notkestrasse 85, 22607 Hamburg, Germany

^dCondensed Matter Physics and Materials Science Department, Brookhaven National Laboratory, Upton, New York 11973, United States

The properties of metal oxide nanoparticles are highly dependent on particle characteristics such as size, crystallinity, and structural defects. To obtain particles with tailor made properties, it is crucial to understand the mechanisms that govern these characteristics during material synthesis. For this purpose, *in situ* studies of particle synthesis have proven powerful.¹ Here, *in situ* Total Scattering (TS) combined with *in situ* PXRD studies of the hydrothermal synthesis of γ -Fe₂O₃ from ammonium iron citrate will be presented. *In situ* TS with Pair Distribution Function (PDF) analysis has recently shown to be an efficient tool for understanding the fundamental chemical processes in particle crystallization.^{2,3} The full γ -Fe₂O₃ crystallization process from ionic complexes over nanoclusters to crystalline particles is followed and material formation mechanisms are suggested. The study shows that the local atomic structure of the precursor solution is similar to that of the crystalline coordination polymer [Fe(H₂cit)(H₂O)]_n where corner sharing [FeO₆] octahedra are linked by citrate. As hydrothermal treatment of the solution is initiated, clusters of edge sharing [FeO₆] units form. Tetrahedrally coordinated iron subsequently appears in the structure and as the synthesis continues, the clusters slowly assemble into nanocrystalline maghemite. The primary transformation from amorphous clusters to nanocrystallites takes place by condensation of the large clusters along corner sharing tetrahedral iron units. The crystallization process is related to large changes in the local structure as the interatomic distances in the clusters change dramatically with cluster growth. The local atomic structure is size dependent, and particles below 6 nm are highly disordered. Whole Powder Pattern Modelling of the PXRD data shows that the final crystallite size (<10 nm) is dependent on synthesis temperature and

that the size distribution of the particles broadens with synthesis time.

[1] Jensen, K.M.Ø.; Tyrsted, C.; Bremholm, M.; Iversen, B. B.; *ChemSusChem*, 2014, doi 10.1002/cssc.201301042

[2] Jensen, K.M.Ø.; Christensen, M.; Juhas, P.; Tyrsted, C.; Bojesen, E.D.; Lock, N.; Billinge, S.J.L.; Iversen, B. B.; *J. Am. Chem. Soc.* 2012, 134, 6785-6792

[3] Tyrsted, C.; Jensen, K.M.Ø.; Bøjesen, E.D.; Lock, N.; Christensen, M.; Billinge, S.J.L.; Iversen, B.B., *Angew. Chem. Int. Ed.* 2012, 51, 36, 9030-9033

Keywords: Pair Distribution Function, *in situ*, nanoparticles

MS08_O2

Strain characterisation in Nano-crystalline ceramics: The Laser pump-probe technique

M. E. Jones^a, S. Fearn^a, R. Winter^a, A. Lennie^b, J. Parker^b, C. Murray^b, S. Thompson^b, C. C. Tang^b & I. Clark^c

^aInstitute of Mathematics and Physics, Aberystwyth University, Wales, SY23 3BZ

^bBeamline I11, Diamond Light Source, Harwell Science and Innovation Campus, England, OX11 0DE.

^cCentral Laser Facility, Rutherford-Appleton Laboratory, Harwell, OX11 0QX

In many applications materials suffer repeated dynamic strain cycles, including various materials ranging from semiconductors (photovoltaic absorber layers) to fuel cell electrolytes and refractory bricks. These cycles of incident strain cause shockwaves which propagate throughout the bulk. These shockwaves can leave behind defect states in the material causing minor residual strain. However, as the number of defect states increases, this *minor* residual strain becomes *significant*^[1].

This experiment utilises the Mythen position sensitive detector on beamline I11 at Diamond to take very short exposures of the sample (1ms) during strain propagation^[2]. Strain was generated in various ceramics and minerals using either a 125W CO₂ laser heating a small part of the sample) or a Nd:YAG laser from the EPSRC Loan pool. The latter causes a shockwave without introducing a heat load on the sample.

The distance of the exposure site from the shock site was varied in order to monitor the effect w.r.t the distance from the shock site. Due to the small number of incident photons available on such short timescales, the experiment is repeated in order to improve statistics. These are then summed to form longer exposures ~1s.

Our results show oscillations in lattice parameters as the dynamic strain accumulates in the sample, once a

particular threshold is reached the strain is released, and this release of energy is due to the failure of grain contact points. The baseline of these oscillations increases over time, suggesting an accumulation of damage in the sample over the duration of the experiment.

These results suggest that a material's resistance to this dynamic strain is predominantly due to the granular structure. Data for various grain shapes, sizes and preferential orientations has been acquired and is currently being analysed.

-
- [1] P. Ballard, J. Fournier, R. Fabbro and J. Frelat. *Journal De Physique III C3-01*, (1991), 487-494
[2] S. P. Thompson, J. E. Parker, J. Potter, T. P. Hill, A. Birt, T. M. Cobb, F. Yuan, and C. C. Tang. *AIP Rev. Sci. Instrum.* (2009), 80, 075107

Keywords: Strain; Zirconia; Shockwave

MS08_O3

In-situ Synchrotron and Neutron Diffraction on Phase Transformations in Austempered Ductile Iron (ADI)

Xiaohu Li^a, Patrick Saal^b, Leopold Meier^{a,b}, Markus Hoelzel^a, Michael Hofmann^a & Wolfram Volk^b

^a *Forschungs-Neutronenquelle FRM II, Technische Universität München, Lichtenbergstr. 1, D-85747 Garching, Germany*

^b *Institute of metal forming and casting, Technische Universität München, Walther-Meißner-Str. 4, D-85747 Garching, German*

Austempered ductile iron (ADI) is a nodular ductile iron which has undergone a special heat treatment to greatly enhance mechanical properties like ductility and yield strength. The heat treatment process of ADI consists of austenitising, quenching to a temperature typically between 250°C and 450°C and isothermal austempering [1]. Alloying elements such as Ni, Mn or Cu are used in industrial applications in order to delay the phase transition kinetics, which is important in practice to improve the austemperability of thicker geometries.

Within the presented work the phase transformation kinetics of three different ADI materials were investigated using neutron and synchrotron diffraction to follow the evolution of phase fraction and lattice parameters characteristics in-situ during the heat treatment. In case of synchrotron diffraction the

samples were heat treated in a dilatometer while for neutron diffraction we used a custom made mirror furnace to reach the fast quenching rates required after the austenisation process of the alloy. After the quenching, austempering followed for 40min to 2.5 hs at selected holding temperatures between 250°C and 450°C.

The diffraction data enable to quantify the changes in phase fraction, austenite carbon enrichment – indicated by changes in lattice parameters – and microstress in austenite and ferrite during austenitising and austempering. The quasi-continuous data also makes it possible to precisely identify the industrial relevant heat treatment window between the maximization of austenite carbon enrichment and the onset of carbide precipitation. Moreover we also report on first neutron diffraction experiments on the behavior of the so prepared ADI alloys under load to investigate possible strain induced transformations of the highly enriched austenite into martensite [2].

-
- [1] L.Meier, M. Hofmann, P.Saal, W. Volk, H. Hoffmann, *Mater. Char.* **85** (2013) 124-133
[2] M.Daber, P. Prasad Rao, *J. Mat. Sci.* **43** (2008) 357-367

Keywords: in-situ diffraction, cast iron, phase transformation, mechanical properties

MS08_O4

Reaction pathways and intermediates in the hydrogenation of Zintl phases by in situ neutron powder diffraction

Holger Kohlmann^a & Patrick Wenderoth^b

^aUniversity of Leipzig, Germany, e-mail: holger.kohlmann@uni-leipzig.de
^bSaarland University, Saarbrücken, Germany

Zintl phases can take up hydrogen to yield polyanionic or Zintl phase hydrides [1]. In the latter hydrogen occupies interstitials as a hydride, H⁻, thus oxidizing the polyanionic Zintl anion. According to the Zintl-Klemm concept this results in an increased connectivity within the polyanion. The opposite is true for polyanionic hydrides, in which hydrogen binds covalently to the polyanion and often inserts into homonuclear bonds, hereby reducing the connectivity of the polyanion. In order to gain insight into reaction pathways and possible intermediates we have studied the hydrogenation (deuteration) of Zintl phases for both types of reactions *in situ* by neutron powder diffraction with a sapphire gas pressure cell [2,3]. SrGa₂ forms a

polyanionic hydride SrGa₂H₂ [4] while CaSi may be hydrogenated to Zintl phase hydrides CaSiH and CaSiH_{1,2} [5]. SrGa₂ does not incorporate deuterium into interstitials, but reacts directly to the polyanionic deuteride SrGa₂D₂ with covalent Ga-D bonds of 186.6(8) pm [2]. Structural parameters are in accordance with [4]. *In situ* neutron diffraction on the deuteration of CaSi reveals the existence of a new intermediate with a structure similar to CaSiD, however, with lower deuterium content corresponding to CaSiD_{0,3}. The reaction from the Zintl phase CaSi to the deuteride CaSiD_{0,3} is very fast and reversible. It completes within less than two minutes at 600 K by changing the deuterium pressure between 1 and 55 bar. The fast kinetics may be of importance for hydrogen storage applications. The hydrogenation of related compounds such as MGa₂ (M = Eu, Yb) and alkaline silicides will also be discussed.

-
- [1] U. Häußermann, V. F. Kranak, K. Puhakainen, *Struct. Bond.* **2011**, 139, 143-162
[2] P. Wenderoth, H. Kohlmann, *Inorg. Chem.* **2013**, 52, 10525-10531
[3] H. Kohlmann, N. Kurtzemann, T. C. Hansen, *Powder Diffr.* **2013**, 28, S242-S255
[4] T. Björling, D. Noréus, U. Häussermann, *J. Am. Chem. Soc.* **2006**, 128, 817-824
[5] H. Wu, W. Zhou, T. J. Udovic, J. J. Rush, T. Yildirim, *Phys. Rev. B: Condens. Matter Mater. Phys.* **2006**, 74, 224101

Keywords: Zintl phases, Zintl phase hydrides, polyanionic hydrides, metal hydrides, *in situ* neutron diffraction, hydrogen storage

Posters:

MS08_P78

In situ high resolution synchrotron X-ray powder diffraction studies of lithium batteries

Mahrez Amri^a, Andy Fitch^b & Poul Norby^c

^aDTU Energy Conversion, Roskilde, Denmark, e-mail: mamr@dtu.dk

^bESRF, Grenoble, France, e-mail: bfitch@esrf.fr

^cDTU Energy Conversion, e-mail: pnor@dtu.dk

Lithium ion batteries have been successful in operating electronic devices such mobile phones and laptops due to their superior capacity compared to other rechargeable battery technologies. However, as our society is moving towards utilisation of sustainable energy sources, batteries can be foreseen to become an even more important part of the energy infrastructure. They will be used not only for transportation, but also for medium and short term storage as well as for frequency stabilisation in intermittent grid scale energy sources such as solar and wind. Thus, the development of new and cheaper battery materials with high energy storage capacity and superior power and energy density is of utmost importance.

The understanding of structural and compositional changes of bulk electrodes in batteries is undoubtedly important. However, it is often transport of electrons and ions across and through interfaces which limits the obtainable power density and battery life time. A challenging and important task is to obtain *in situ* information about the interfaces in an operating battery. In the FP7 project Hi-C (Novel *in situ* and *in operando* techniques for characterisation of interfaces in electrochemical storage systems) we will address these challenges.

One of the tasks in the Hi-C project is to study intraparticle interfaces, *e.g.* between lithiated and non-lithiated domains inside electrode micro- and nanocrystallites during charge and discharge. We are using *in situ* high resolution synchrotron X-ray powder diffraction to obtain detailed structural and compositional information during lithiation/delithiation of lithium ion batteries. A special capillary-based battery cell has been developed^[1], allowing diffraction information to be obtained from only the active material during operation.

We report results from the first *in situ* time resolved high resolution powder diffraction experiments at

beamline ID31 at the European Synchrotron Radiation Facility, ESRF. We follow the structural changes during lithiation/delithiation of a LiFePO₄ based battery cell using Rietveld refinement.

[1] Rune E Johnsen and Poul Norby, *Journal of Applied Crystallography*. 2013, 46, 1537.

Keywords: Lithium batteries, x-ray powder diffraction, micro capillary battery cell

MS08_P79

Formation and Growth of Magnetic γ -Fe₂O₃ Nanocrystallites under Hydrothermal Conditions

Henrik L. Andersen^a, Kirsten M. Ø. Jensen^{a,b}, Christoffer Tyrsted^a, Espen D. Bøjesen^a & Mogens Christensen^a

^aAarhus University, Denmark

^bColumbia University in the City of New York, USA
e-mail: lyder@chem.au.dk

Magnetic iron oxide nanoparticles are of key importance in a broad range of scientific and technological applications, including permanent magnets, magnetic fluids, biomedicine, data storage and catalysis.[1-4] The properties of maghemite are highly dependent on particle size, size distribution, morphology, and particle aggregation. Maghemite (γ -Fe₂O₃) in the bulk form is ferrimagnetic at room temperature. However, reducing the size of the maghemite nanoparticles below the superparamagnetic limit, results in zero magnetization at room temperature, due to random spin reorientation in zero field conditions. In recent years, an increasing effort has been put into developing synthesis methods in which these characteristics are tuneable to meet the requirements of the various applications.

The formation and growth of maghemite nanocrystals during the hydrothermal synthesis from aqueous solutions of ammonium iron(III) citrate (C₆H₈O₇·xFe(III)·yNH₃) have been studied by *in situ* powder X-ray diffraction (PXRD). Data analysis by Rietveld refinement and whole powder pattern modelling (WPPM) reveals that the crystallite size and size distributions can be precisely tuned through simple adjustments of the reaction temperature and time.[5] Increasing the reaction temperature causes faster growth and results in larger crystallites while the size distributions broaden as reaction times increase, regardless of temperature.

- [1] Lu, A. H., Salabas, E. L., Schuth, F., *Angewandte Chemie, International Edition*. 2007, 46, 1222-1244.
[2] Pankhurst, Q. A., Connolly, J., Jones, S. K., Dobson, J., *Journal of Physics D: Applied Physics*. 2003, 36, R167-R181.
[3] Vekas, L., *Smart Materials & Micro/Nanosystems*. 2009, 54, 127-136.
[4] Doudrick, K., Yang, T., Hristovski, K., Westerhoff, P., *Applied Catalysis, B: Environmental*. 2013, 136, 9-18.
[5] Andersen, H. L., Jensen, K. M. Ø., Tyrsted, C., Bøjesen, E. D., Christensen, M., *Crystal Growth & Design*. 2014, 14, 1307-1313.

Keywords: Maghemite, nanocrystallites, in situ, powder diffraction, hydrothermal, size distribution, Rietveld, whole powder pattern modeling.

MS08_P80

Time-resolved structural characterization of fluoride cathode materials by *in situ* microdiffraction analysis

L. de Biasi^{a,b}, G. Lieser^a, J.R. Binder^a, R. Mönig^{a,b} & H. Geßwein^{a,b}

^aKarlsruhe Institute of Technology (KIT), Germany,

^bHelmholtz Institute Ulm (HIU), Germany
e-mail: lea.biasi@kit.edu

Repetitive insertion and extraction of Li ions during cycling of a lithium ion battery (LIB) can be accompanied with significant lattice parameter changes and phase transformations within the electrode materials. Affecting the crystal structure as well as the microstructure of the active material these changes are considered to be responsible for undesirable material degradation associated with capacity loss and reduction of operation life time [1]. A suitable method to detect and evaluate the insertion mechanisms and their impact on the crystalline electrode structure is X-ray powder diffraction.

Changes in the crystal structure of two potential LIB cathode materials of type LiM^{II}M^{III}F₆ (M^{II}=Mn,Ni and M^{III}=Fe) were evaluated by *in situ* laboratory X-ray microdiffraction during galvanostatic cycling. The flexible *in situ* X-ray diffractometer consists of a Mo microfocus rotating anode with a 2D collimating multilayer optic which allows high photon flux and the investigation of the cathode material within an electrochemical coin cell in transmission mode. A fast 2-dimensional Pilatus 300K-W detector is used to collect whole portions of the Debye-Scherrer rings at once. Due to the good counting statistics of the 2D diffraction patterns a time resolution of several minutes can be achieved. With the aid of the Rietveld method detailed structural and microstructural information can be extracted from the integrated 1D diffraction patterns.

The obtained structural information can then be directly related to the electrochemical recordings of the simultaneously performed galvanostatic measurements. Compounds of type $\text{LiM}^{\text{II}}\text{M}^{\text{III}}\text{F}_6$ exhibit different crystal structures depending on the ratio of metal ion radii $r_{\text{MII}}/r_{\text{MIII}}$ [2]. LiMnFeF_6 crystallizes in a Na_2SiF_6 -type lattice ($P321$) whereas LiNiFeF_6 features a trirutile-type structure ($P4_2/mnm$). The performed *in situ* XRD experiments reveal a structure dependence of the lithium insertion mechanisms arising from the different initial host lattice types of the two cathode materials.

[1] P. Arora, R.E. White and M. Doyle, *J. Electrochem. Soc.* 1998, 145, 3647-3667. [2] W. Viebahn, 1977, 140.

Keywords: in situ XRD, lithium ion battery, fluoride

MS08_P81

In situ study of hydrothermal MnO_2 formation

Steinar Birgisson^a, Yanbin Shen^a & Bo Brummerstedt Iversen^a

^aAarhus University, Denmark, e-mail: steinar@eng.au.dk

Our group has designed and successfully implemented an experimental setup capable of *in situ* measurements of solvothermal reactions. The setup uses synchrotron radiation and a time resolution in the range 1-10 seconds can be acquired [1]. The experiments can be optimized either to measure powder X-ray diffraction (PXRD) data or total scattering (TS) data. From PXRD data properties such as what crystalline phases are present and their weight fractions, structural parameters (e.g. unit cell parameters, site occupancies, bond lengths), crystallite sizes and morphologies are extracted as a function of reaction time using Rietveld refinements [2]. TS data gives information about all the material in the solution; from complexes to amorphous particles to crystalline particles. Properties such as bond lengths, scale factors and particle sizes as a function of reaction time can be extracted via real space refinements of structural models [3].

Manganese dioxide forms a variety of phases that can have tunnel like structures, such as alpha, beta and gamma, or layered structure, such as delta. Many of these phases have shown potential for use in various applications such as a catalyst, electrode material in supercapacitors and positive electrode material in lithium batteries (both primary and secondary) [4, 5]. In this study we investigate the hydrothermal formation of different phases of MnO_2 *in situ* using the experimental

setup described above. Alpha-, beta- and delta- MnO_2 are synthesized from different aqueous precursor solutions at different temperatures ranging from subcritical to supercritical conditions. Measurements are done to obtain both PXRD and TS data. Therefore information about reaction mechanism from precursor solution (containing dissolved species) to final crystalline product can be extracted along with yield and particle growth as a function of reaction time. Measurements at different temperatures provide information on the temperature dependence of the reaction kinetics and activation energies of the reactions.

[1] Becker et al, *J. Appl. Crystallogr.* 2010, 43, 729-736
[2] (a) Jensen et al., *Angew. Chem.* 2007, 46, 1113-1116; (b) Bremholm et al., *Angew Chem.* 2009, 48, 4788-4791; (c) Bremholm et al., *Adv. Mater.* 2009, 21, 3572-3575; (d) Lock et al, *Angew Chem.* 2011, 50, 7045-7047; (e) Nørby et al., *RSC Adv.* 2013, 3, 15368; (f) Eltzholtz et al., *Nanoscale* 2013, 5, 2372
[3] (a) Jensen et al., *J. Am. Chem. Soc.* 2012, 134, 6785-6792; (b) Tyrsted et al, *Angew. Chem.* 2012, 51, 9030-9033
[4] M. M. Thackeray, *Prog. Solid St. Chem.* 1997, 25, 1 - 71
[5] Qiu et al, *Chem. Mater.* 2011, 23, 3892-3901

Keywords: In situ, Powder X-ray Diffraction, Total scattering, Manganese Dioxide, Battery

MS08_P82

In- and ex situ PXRD studies of the influence of various synthesis parameters on the growth of ZnO nanoparticles in sub-critical water

Espen D. Bøjesen^a, Kirsten M. Ø. Jensen^{a,b}, Christoffer Tyrsted^a, Nina Lock^{a,c}, Mogens Christensen^a & Bo B. Iversen^a

^aCenter for Materials Crystallography, Department of Chemistry and iNANO, Aarhus University, DK-8000 Aarhus C, Denmark, espen@chem.au.dk
^bApplied Physics and Applied Mathematics, Columbia University, New York, New York 10027, United States

^cDept. of Inorganic Chemistry, Georg-August-Universität Göttingen, D-37077 Göttingen, Germany

Zinc oxide (ZnO) is a material which has attracted great scientific interest, due to the plethora of technologically relevant physical properties it exhibits despite its simple structure, low toxicity and low production cost. It is used widely in all sorts of applications. Synthesis of ZnO nanoparticles can be performed by a wide assortment of methods resulting in a tremendous variety of sizes and shapes. Previous *in situ* characterization methods have investigated the ZnO formation under various synthesis conditions; including numerous spectroscopic methods and small angle scattering. Common characteristics for all these studies is that the primary focus has been to extract information on

particle size and shape of ZnO, while a more rigorous microstructural and structural analysis has been lacking. Furthermore, the aforementioned studies have primarily focused on soft chemical synthesis methods, at low temperatures and in non-aqueous media. The widely used environmentally benign and versatile hydrothermal method has basically been omitted.

In the present work the formation of ZnO during hydrothermal synthesis has been followed using *in situ* powder X-ray diffraction (PXRD) combined with Rietveld refinement, thus enabling extraction of crystallographic and microstructural information during the formation and growth of ZnO. Supporting *ex situ* syntheses and characterization by electron microscopy, high resolution PXRD and other techniques have been used to corroborate the findings from the *in situ* experiments. Mapping out a vast parameter space has led to a deeper understanding of the intricate mechanisms governing the nucleation and growth of ZnO nanoparticle during hydrothermal synthesis. Among the parameters studied were the influence of temperature, type of base used and the influence of different ionic salts as synthesis directing agents. The various synthesis parameters were found to influence the following structural and microstructural features: crystallite shape, morphology and size as well as the twin-fault concentration, degree of doping and crystallinity.

Keywords: Nanoparticles, Microstructure, In situ, Zinc oxide

MS08_P83

Synchrotron X-ray diffraction study of thermal decomposition of expanded austenite

Bastian Brink^a, Kenny Ståhl^b, Thomas L. Christiansen^c & Marcel A. J. Somers^d

^aTechnical University of Denmark, e-mail: basbr@mek.dtu.dk, ^bkenny@kemi.dtu.dk, ^ctch@mek.dtu.dk, ^dsomers@mek.dtu.dk

Expanded austenite is produced from low temperature nitriding (<720 K), carburizing (<820 K) or nitrocarburizing of austenitic stainless steel [1]. This introduces nitrogen/carbon into the surface adjacent region and improves wear and fatigue performance. The surface hardness can be increased by an order of magnitude, while corrosion resistance is retained and may even be improved by the process.

In the present work *in-situ* synchrotron X-ray diffraction was applied to investigate thermal expansion and thermal stability of expanded austenite in the temperature range 385 - 920 K. Samples were produced from AISI 316 grade stainless steel powder by gaseous nitriding in ammonia/hydrogen gas mixtures or carburizing in acetylene/hydrogen or propene/hydrogen gas mixtures.

The highest obtained nitrogen content corresponds to an occupancy of the octahedral voids of $y_N=0.56$. Previous EXAFS studies have shown Fe, Cr and Ni exist in different local environments with short range ordering between Cr and N [2]. As diffraction peaks do not fit ideally to FCC positions, a stacking fault probability was included as a fitting parameter in Rietveld refinements. The stacking fault probability is constant for temperatures up to 680 K, thereafter it decreases to nil. For nitrogen expanded austenite the decomposition products and the coefficient of thermal expansion depend on the initial nitrogen content. For high nitrogen contents a transitional FCC phase appears at temperatures above 770 K with lattice parameter $a \approx 3.8$ Å ($y_N=0.25$), suggesting a M_4N phase $M=(Fe,Cr,Ni)$.

For carbon expanded austenite no stacking fault induced peak shifts were observed and decomposition produces first χ - M_5C_2 carbide which at higher temperatures is transformed to M_7C_3 .

[1] T.L. Christiansen and M.A.J. Somers. *Metall. Mater. Trans A*. 2006, 37, 675-682. [2] J. Oddershede, T.L. Christiansen, K. Ståhl and M.A.J. Somers. *Scripta Mater.* 2010, 62, 290-293.

Keywords: expanded austenite, in-situ, thermal decomposition

MS08_P84

X-ray powder diffraction applied to cement related phases: in-situ and high resolution applications

Ana Cuesta^a, Gema Álvarez-Pinazo^a, Ángeles G. De la Torre^a, Isabel Santacruz^a, Inma Peral^b & Miguel Ángel G. Aranda^b

^a Departamento de Química Inorgánica, Cristalografía y Mineralogía, Universidad de Málaga, 29071 Málaga, SPAIN

^b ALBA Synchrotron radiation facility, . Ctra. BP1413 km 3.3, 08290 Cerdanyola del Vallès, Barcelona, SPAIN
email: a_cuesta@uma.es

XRPD is a powerful tool for material characterization in general, and for *in-situ* studies of chemical processes in particular. The use of an intense X-ray source, .i.e. synchrotron X-rays, coupled with fast X-ray detection permits time-resolved diffraction experiments allowing

in-situ quantitative phase analysis during the early ages of cement hydration.

CSA cements may have variable compositions, but all of them contain ye'elimite ($\text{Ca}_4\text{Al}_6\text{O}_{12}\text{SO}_4$). This phase is also included, ~25 wt%, in sulfobelite cements. Also, another important phase in these cements is tetracalcium aluminoferrite ($\text{Ca}_2\text{AlFeO}_5$).

The aim of this work is to better understand the early age hydration of stoichiometric (orthorhombic) and doped (pseudo-cubic) ye'elimite and tetracalcium aluminoferrite phases at early ages in order to understand "eco-cement" performances. Chiefly, we want to determine the hydration kinetic and mechanisms of these phases with different water/cement ratio, with different calcium sulfate sources.

This work has allowed establishing kinetics and mechanisms for hydration of ye'elimite samples by *in-situ* SXRPD with internal standard methodology. Moreover, some pastes were studied by *ex-situ* LXRPD with the external standard method, G-factor, at 2 and 7 days. Both strategies were able to quantify the amorphous contents, including free water. It is important to highlight that the results obtained by the internal standard method are in agreement with those obtained at later ages showing the consistence of both methodologies to follow hydration reactions with time by diffraction methods. Moreover, the hydration of tetracalcium aluminoferrite and some combinations of this phase with ye'elimite have been studied by *in-situ* SXRPD in order to understand the dissolution/crystallization processes that take place during those hydration processes.

Furthermore, we have measured some hydrated phases by high resolution SXRPD in order to perform a structural study with the objective of revising or obtaining the crystal structure descriptions.

[1] A. Cuesta, A. G. De la Torre, E. R. Losilla, V. K. Peterson, P. Rejmak, A. Ayuela, C. Frontera and M. A. G. Aranda, *Chem. Mater.* 2013, 25, 1680

Keywords: Hydration studies, LXRPD & SXRPD

MS08_P85

In situ XRPD and quantitative analysis of simplified cement pastes: estimating the amorphous fraction by standard-less methods

[Maria Chiara Dalconi](#)^{a,b}, [Luca Valentini](#)^{a,b}, [Marco Favero](#)^{a,b},
[Gilberto Artioli](#)^{a,b} & [Giorgio Ferrari](#)^c

^aDepartment of Geosciences, University of Padua, Italy, e-mail: mariachiara.dalconi@unipd.it.

^bCIRCe Centre for the study of cement materials, University of Padua, Italy.
^cR&D department, Mapei SpA, Milan, Italy, e-mail: g.ferrari@mapei.it

The hydrating cement paste is a multiphase system in which crystalline and amorphous components take part to the hydration process. *In situ* x-ray diffraction (XRD) has revealed to be a powerful technique to track the phase evolution during hydration. However, only the crystalline components can be directly observed whereas the amorphous components are almost undetectable by XRD.

For cement pastes, the amorphous components (mainly unbound water and C-S-H) can be derived from Rietveld relative phase fractions on the basis of mass balance calculation assuming constant reaction stoichiometry. As an alternative approach, the external standard method of O'Connor and Raven [1] (also indicated as the G-factor method) has been successfully applied to calculate the absolute content of the crystalline and amorphous phases.

Here we re-propose an alternative approach [2, 3] to quantify both the crystalline and the amorphous components of hydrating C3S paste from *in situ* diffraction data measured in capillary-transmission geometry. The proposed method uses the known amount of C3S in the paste at the beginning of hydration as an internal standard.

In addition, a mass balance algorithm (implemented in the RieCalc program) [4], which can discriminate between C-S-H and capillary water, is presented. The comparison between the results derived from the two methods provides information about the stoichiometry of C-S-H formed by the reaction of C3S hydrated in the presence or absence of gypsum.

[1] B.H. O'Connor, M.D. Raven, *Powder Diffr.* 1988, 3 (1), 2-6.

[2] M. Merlini, G. Artioli, T. Cerulli, A. Bravo, F. Cella, *Cem. Concr. Res.* 2008, 38, 477-486.

[4] C. Hesse, F. Goetz-Neunhoeffer, J. Neubauer, *Cem. Concr. Res.* 2011, 41, 123-128.

[3] L. Valentini, *J. Appl. Cryst.* 2013, 46, 1899-1902.

Keywords: hydrating cement paste, Rietveld quantitative analysis, *in situ* XRPD, RieCalc.

Understanding the flexibility of MOFs: a combined powder synchrotron and neutron powder diffraction and solid state NMR study

Damien Foucher^{a,b,c}, Francis Taulelle^a, Florence Porcher^b, Erik Elkaim^c & Charlotte Martineau^a

^aTestospin, Institut Lavoisier, UMR CNRS 8180, Université de Versailles St-Quentin-en-Yvelines, 78035 Versailles, France

^bLaboratoire Léon Brillouin, CEA-CNRS, CEA-Saclay, 91191 Gif-sur-Yvette cedex, France

^cSoleil Synchrotron, 91192 Gif-sur-Yvette, France

'Metal-organic-frameworks' (MOFs) are porous materials with exceptional properties in domains like gas adsorption/separation, catalysis, drug-delivery... The structure of these MOFs is built up from metal clusters connected together by organic linkers, forming 3D frameworks with variable pore size and geometry¹. Some of these solids have extremely flexible structures. For example, in the MIL-53 family, structural transitions from an 'open-pore' phase to a 'closed-pore' phase were observed. This phenomenon, sometimes called the breathing effect, is accompanied by lattice parameter (thus pore volume) variations up to 40%. The main factors responsible for the breathing effect are the temperature^{2,3} and/or the pressure and nature of guest species contained in the pores⁴ (water, gas ...).

In this contribution, we report a study of the flexibility of diamagnetic MOFs by combining experimental data from powder synchrotron and neutron diffraction along with solid-state nuclear magnetic resonance (NMR) spectroscopy. We make use of the complementary length-scale sensitivity that provide these techniques to get insights into the role of water and temperature on the MOF flexibility.

[1] C. Serre, F. Millange, G. Férey, *J. Am. Chem. Soc.* 2002, 124, 13519-13526 [2] Y. Liu & al., *J. Am. Chem. Soc.* 2008, 130, 35 [3] M. Mendt, *J. Phys. Chem. C* 2010, 114, 45 [4] S. Bourelly & al, *J. Am. Chem. Soc.* 2005, 127, 13519-13521

Keywords: XRPD, NPD, solid state NMR, MOFs, flexibility, water, synchrotron

The influence of petrography on the thermal decomposition and burnability of limestones used in industrial cement clinker

Matteo Galimberti^a, Nicoletta Marinoni^a, Maurizio Marchi^b & Giovanna Della Porta^a

^aUniversity of Milan, Italy, e-mail: matteo.galimberti@unimi.it
^bCTG – Italcementi Group, Bergamo, Italy

In this study the influence of the petrography on the thermal decomposition and burning behaviour of five different limestones, the main raw materials for ordinary Portland cement clinker, have been investigated.

The samples were first examined by transmitted light optical microscopy in order to determine micrite to sparite ratio and their distribution. Then, the study of limestone thermal decomposition was conducted under isothermal conditions by means of in situ High Temperature X-Ray Powder Diffraction [1].

Five kiln feeds were then prepared and submitted to burning trials and later the main phases were quantified by the Rietveld method and investigated by Scanning Electron Microscopy [2].

The results attest that petrography has a fundamental role during the thermal decomposition of the selected limestones as well as it considerably influences how the raw materials react each other to produce the main clinker phases. Especially, the micrite to sparite ratio seems to be the driving feature for the decomposition and burnability of the different limestones. The limestone with the lowest micrite to sparite ratio shows the lowest E_a value and the highest calcination rate indeed, factors that both lead to a high burnability of the raw mix.

[1] Marinoni et. Al, *J. Am. Ceram. Soc.*, 95, 2491-2498 [2] Taylor H.F.W., *Cement chemistry*, Thomas Telford, London 1990

Keywords: limestone, kinetics, clinker, in situ X-Ray Powder Diffraction, Rietveld method

Phase transition behavior of elemental substituted high voltage spinel cathodes studied by *in situ* XRD

Holger Geßwein^{a,b}, Sven Glatthaar^a, Lea de Biasi^{a,b}
& Joachim R. Binder^a

^aKarlsruhe Institute of Technology, Germany, ^bHelmholtz Institute Ulm (HIU), Germany

e-mail: holger.gesswein@kit.edu

High voltage spinel $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ [1] is a well-known cathode material for lithium-ion batteries that operates at high voltage of about 4.7V vs Li/Li^+ . Besides the high energy density the spinel structure offers an intrinsically fast Li^+ diffusion within the three-dimensional structure leading to a high rate capability of this material. However the electrochemical properties of $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ are very sensitive to the synthesis route, the calcination temperature and elemental substitution of the transition metals or the partial substitution of oxygen with the more electronegative fluorine [2]. Synchrotron based *in situ* characterization techniques are powerful tools to understand the effects of the chemical modifications of the host structure and to reveal the underlying reaction mechanisms which can include several phase transitions during battery operation.

In this work we present an *in situ* X-ray diffraction study on a series of cation and anion substituted spinel materials including Fe, Fe/F, Fe/Ti and Fe/Ti/F modified $\text{LiNi}_{0.5}\text{Mn}_{1.5}\text{O}_4$ spinel. It is shown that the elemental substitution changes the electrochemical behavior and the accompanied 2-phase and solid-solution reactions in the high voltage plateau and during deep discharge when more than 1 Li is inserted into the spinel structure and the cubic spinel transforms to a tetragonal modification. Furthermore the cycling behavior at higher cycle numbers is presented.

[1] Yi, T.-F. et. al; *Ionic*s, 2011, 17, 383-389

[2] Liu, J. and Manthiram, A, *J. Phys. Chem. C*, 2009, 113, 15073-15079

Keywords: Lithium-ion battery, high voltage spinel, *in situ* SXRD

In situ crystallization of $\text{SrFe}_{12}\text{O}_{19}$

Cecilia Granados-Miralles^a, Matilde Saura-Múzquiz^a, Espen D. Bøjesen^a, Kirsten M. Ø. Jensen^{a,b} & Mogens Christensen^a

^aCenter for Materials Crystallography, Department of Chemistry and iNANO, Aarhus University, Denmark

^bApplied Physics and Applied Mathematics, Columbia University, New York, United States

e-mail: granados@chem.au.dk

Magnets are key components in many electronic devices as well as basis of state-of-the-art biomedical applications such as magnetically-guided drug delivery systems (DDS). For these purposes, materials are required to be both biocompatible and nano-sized.

$\text{SrFe}_{12}\text{O}_{19}$ is an inexpensive choice that meets the mentioned needs besides offering good magnetic performance.

Hydrothermal synthesis is widely known to be a quick, clean and up-scalable method for producing nanoparticles, and it allows high control over the reaction parameters.

In this study, hydrothermal synthesis of $\text{SrFe}_{12}\text{O}_{19}$ was monitored using powder diffraction and synchrotron radiation ($\lambda = 1.0 \text{ \AA}$, I711 MAX-II, Lund University, Sweden). The powder diffraction patterns were collected with a time-resolution of 5 seconds. Subsequent Rietveld analysis of the data provided extensive knowledge about the reaction kinetics, growth mechanisms, crystallite size and morphology dependence on reaction time and temperature. The data show how a crystalline $\text{SrFe}_{12}\text{O}_{19}$ phase grows from an initial amorphous precursor, when submitted to high pressure and temperature.

Additionally, we have identified an intermediate phase, which develops into $\text{SrFe}_{12}\text{O}_{19}$ when hydrothermally treated for long enough time. This phase has been mistaken to be tiny incipient crystals of $\text{SrFe}_{12}\text{O}_{19}$ in previous literature. The insight obtained from *in situ* diffraction studies allows us a much better control of preparing phase pure $\text{SrFe}_{12}\text{O}_{19}$ in subsequent *ex situ* experiments.

Keywords: *in situ*, powder x-ray diffraction, hydrothermal synthesis, permanent magnets

MS08_P90

Mechanistic Information about Copper/Ceria CO Oxidation Catalyst Obtained from Pulsed Reactants and Phase Sensitive Detection

J. C. Hanson^a, A. A. Yakavenko^a, G. Tutuncu^a, S. D. Senanayake^a, K. Mudiyansele^a, J.A. Rodriguez^a, A. Martínez-Arias^b & E. Dooryhee^a

^aBrookhaven National Laboratory, Upton, NY, USA, ^bInstituto de Catálisis y Petroleoquímica, CSIC, Madrid, Spain, e-mail: hanson1@bnl.gov

A unique copper/ceria catalyst which is designed to maximize the amount of interface between CuO_x and ceria has been shown to have preferential oxidation (PROX) of CO in the presence of hydrogen. This catalyst is composed of 60% CuO and 40% CeO₂. It has been developed to purify input to fuel cells [1]. Preliminary pulsed oxidation/reduction studies on this catalyst have established relative reactivity of the copper and cerium oxides [2]. In an attempt to understand the mechanism of selective oxidation on this catalyst, the diffraction, infrared (DRIFTS) and the reaction products were measured simultaneously. The Phase Sensitive Detection (PSD) analysis [3] and Modulation Enhanced Diffraction (MED) analysis [4] have been applied to the pulsed data. The pulsed data in the first experiment was an alternation between CO and O₂. In addition, to simulate CO-PROX in the presence of H₂ a second experiment alternated 5% H₂ and 5% O₂ in a constant flow of CO/O₂ 1:1. The PSD analysis of the diffraction data shows the sequential appearance of Cu, Cu₂O and CuO phases during the formation of CO₂ and H₂O. This is to be correlated with the occurrence of CO-Cu⁺ IR absorption and the relative amounts of CO₂ and H₂O. The PSD analysis was essential to observing the small changes in the CuO_x. Parallel measurements have been obtained on traditional catalyst made up of 5% CuO_x on ceria and they provide additional information about the mechanism

This work is supported by the BNL LDRD program and DOE contract DE-AC02-98CH10886. Measurements were carried out at the NSLS and APS synchrotrons and were supported by the US Department of Energy. Thanks to Mr. A. López Cámara from the ICP-CSIC (Spain) for preparation of the samples. Financial support from Ministerio de Economía y Competitividad (project CTQ2012-32928) is acknowledged

[1] Hornes, A., et al., *Journal of the American Chemical Society*, 2010, 132, 34-35

[2] Hanson, J.C., et al., 2014, *Catalysis Today*, <http://dx.doi.org/10.1016/j.cattod.2013.10.087>

[3] Urakawa, A., T. Burgi, and A. Baiker, *Chemical Engineering Science*, 2008, 63, 4902-4909

[4] Chernyshov, D., et al., *Acta Crystallographica Section A*, 2011, 67, 327-335

Keywords: In situ, Catalysis, Phase Sensitive Detection

MS08_P91

In situ X-ray diffraction studies of apatite nanocrystal formation from an amorphous precursor in water.

Casper Ibsen^a, Hanna Leemreize^a & Henrik Birkedal^a

^aDepartment of Chemistry & iNANO, Aarhus University, Aarhus, Denmark, e-mail: hbirkedal@chem.au.dk

The formation of crystals from solution remains far from understood despite many years of research. Crystallization from amorphous precursors is a major pathway in many systems. One of these is hydroxylapatite, Ca₅(PO₄)₃(OH), found in bone. Herein, we use *in situ* synchrotron X-ray diffraction to follow the formation of apatite nanocrystals from amorphous calcium phosphate in water. The introduction of carbonate ions into the amorphous phase significantly influenced the crystallization kinetics and even a simple exchange of counter ion, K⁺ for Na⁺, had a profound impact on the crystallization behavior. Diffraction experiments were performed *in situ* with sub-10 s time resolution using a custom high thermal stability cell [1]. Rietveld refinement allowed following the amount of crystalline material, the average nanocrystal size and the lattice constants over time. At early times, we observed amorphous scattering from the precursor, which gradually disappeared as nanocrystalline apatite formed [1,2].

The crystallites were almost spherical just after nucleation. They grew rapidly along the crystallographic *c*-direction to form needle-like crystals and then matured further through Ostwald ripening. At lower starting pH, the initial crystal shape was not spherical but anisotropic at the earliest time particles were detected. Compressive and expansive strains of the *c*- and *a*-lattice parameters respectively, were present at early times which relaxed throughout the growth period. Exchanging counter-ions (K⁺ instead of Na⁺) lead to slower crystallization and different particle sizes and shapes. This was attributed to the lack of sodium co-substitution of dissolved carbonate ions.

Adding potassium carbonate as an additive stabilized the amorphous phase dose-dependently. Likewise, a reduction of the crystal sizes accompanied by an

asymmetric change of the lattice parameters was observed.

Taken together these results provide insight into growth dynamics of anisotropic crystals showing how a range of factors may influence crystallization behavior including supposedly innocent counter ions.

-
- [1] C. S. Ibsen and H. Birkedal, *J. Appl. Cryst.* 2012, 45, 976-981
[2] C. S. Ibsen and H. Birkedal, *Nanoscale* 2010, 2, 2478-2486

Keywords: Crystallization, In situ, Apatite

MS08_P92

Temperature and time evolution of microstructure of ECAP processed Cu-Zr studied by in-situ powder diffraction

[Radomír Kužel^a](#), [Alžběta Kadlecová^a](#), [Zdenek Matěj^a](#), [Miloš Janeček^b](#) & [Jitka Stráská^b](#)

*Charles University, Faculty of Mathematics and Physics,
^aDepartment of Condensed Matter Physics,
^bDepartment of Physics of Materials
CZ-121 16 Prague, Czech Republic*

Samples of copper and mainly copper with addition of zirconium (0.18 wt. %) processed by equal-channel angular pressing (ECAP) were studied by in-situ high-temperature X-ray powder diffraction (XRD). The stability of fine-grained deformed microstructure decreases with the number of passes (1, 2, 4, 8, respectively) for both series of samples. The addition of zirconium improved the stability from the region of only slightly above 100 °C to about 400 °C. Anomalous diffraction profiles with sharp peak and long tails as well as 2D diffraction patterns indicated the presence of multimodal microstructure leading to wide and narrow components of diffraction profiles. Therefore, bimodal microstructure model was used for the evaluation and whole measured diffraction patterns were fitted by the software MSTRUCT as a sum of two copper phases with different microstructure. It appeared that two factors had main influence on the diffraction profiles and, consequently, could be reliably determined from the experiment – microstrain - dislocation density in the deformed component and the ratio of deformed and recovered fractions. In temperature dependence, slow decrease of dislocation densities in the whole temperature region was observed while significant drop of deformed fraction appeared above 320 °C and higher temperatures for CuZr samples. The latter behaviour was similar to the dependence of microhardness.

Detailed studies of time dependences were performed for Cu-Zr samples at 370 °C, the temperature selected when the microstructural changes are not too fast to be studied in-situ in laboratory X-ray equipment and also samples prepared by different number of ECAP passes can be compared. The development of both fractions could be well observed and described quite well by the JMAK [1-3] equation but with extremely low exponent. Post annealing studies by both XRD and EBSD showed that nearly no grain growth occurred after annealing for tens of hours at this selected temperature and the fraction giving narrow diffraction peaks did not show crystallites essentially larger than in as-deformed grains. Anyway, the bimodal microstructural model seems to be appropriate also in this case since the recovery and recrystallization is not homogenous in Cu-Zr samples.

-
- [1] A. N. Kolmogorov, *Bull. Acad. Sci. U.S.S.R. Phys. Ser.*, 1937, 3, pp. 355-359.
[2] A. M. Johnson, R. F. Mehl, *Trans. Am. Inst. Min. Engrs.* 135 1939, pp. 416-458.
[3] M. Avrami, *J. Chem. Phys.* 9, 1941, pp. 177-184.

Keywords: equal-channel angular pressing, time evolution of microstructure, thermal stability, Cu-Zr

MS08_P93

X-ray powder diffraction applied to study the effect of calcium sulfate source on the hydration of calcium sulfoaluminate eco-cement.

[Laura León-Reina^{a,b}](#), [Marta García-Maté^a](#), [Ángeles G. De la Torre^a](#), [Enrique R. Losilla^a](#), [Miguel A. G. Aranda^c](#) & [Isabel Santacruz^a](#)

*^aDepartamento de Química Inorgánica, Cristalografía y Mineralogía and
^bLaboratorio de Difracción de Rayos-X, SCAI,
Universidad de Málaga, 29071 Málaga, SPAIN
^cALBA Synchrotron radiation facility, Ctra. BP1413 km 3.3, 08290
Cerdanyola del Vallès, Barcelona, SPAIN
email: lauralr@uma.es*

The manufacture of Calcium SulfoAluminate (CSA) cements is more environmentally friendly than that of OPC as their production releases up to 40% less CO₂ than the latter. The main performances of CSA cements are fast setting time (followed by a rapid hardening), good-chemical resistance properties and, depending on the amount of the added sulfate source they are self-levelling materials or shrinkage controllers.

CSA cements present a wide range of phase assemblages, but all of them contain over 50 wt% calcium sulfoaluminate (also known as ye'elimite or

In situ SR-PXD studies of eutectic melting borohydrides

Morten B. Ley^a, Elsa Roedern^a, Pascal Schouwink^b & Torben R. Jensen^a

^aCenter for Materials Crystallography (CMC), Interdisciplinary Nanoscience Center (iNANO) and Department of Chemistry, Aarhus University, Denmark

^bLaboratory of Crystallography, DPMC-MANEP, University of Geneva, 24, Quai Ernest-Ansermet, CH-1211 Geneva, Switzerland
e-mail: ley@inano.au.dk

Klein's salt), jointly with belite, ferrite and other minor components. It is possible to modify the hydration process of CSA cements not only by its composition, but also by the selection of different quantities or sources of calcium sulfate (gypsum, bassanite and anhydrite).

XRPD is a powerful tool for materials characterization in general, and for *in-situ* studies of cements chemical processes in particular. The use of transmission geometry coupled with fast X-ray detection was used to study the *in-situ* hydration¹ of fresh pastes during the early ages of cement hydration (first three hours). Moreover, the pastes were studied by *ex-situ* LXPDP with the external standard method, G-factor, at 1, 3, 7, 28 and 180 days (after stopping hydration) allowing the quantification of the amorphous contents, including free water.

The aim of this work is to study the effect of different sulfate sources on the hydration of CSA cements at early ages, including the evolution of phase assemblages, rheological behavior (very early ages), evolved heat and microstructure.

This work has allowed establishing kinetics and mechanisms for hydration by *in-situ* LXPDP. It is important to highlight that the dissolution rate of the different studied sulfate sources (gypsum, bassanite and anhydrite) is a key point to control the reactions during hydration of CSA cements, and hence the mechanical properties of the corresponding pastes and mortars.

Furthermore, it has been noted that the ettringite contents determined by RQPA and the G-method justify the compressive strength values of the corresponding mortars.

[1] G. Álvarez-Pinazo, A. Cuesta, M. García-Maté, I. Santacruz, E. R. Losilla, S. G. Sanfélix, F. Fauth, M. A. G. Aranda, A. G. De la Torre. *In-situ* early-age hydration study of sulfobelite cements by synchrotron powder diffraction. *Cement and Concrete Research* 2014, 56, 12-19

Keywords: Hydration studies, LXPDP, G-method

Eutectic melting occurs in several mixtures of alkali and alkaline earth metal borohydrides.¹ Here, we examine new eutectic metal borohydrides mixtures, $x\text{LiBH}_4 - 1-x\text{KBH}_4$ ($x = 0.7 - 0.75$) and $\text{Y}(\text{BH}_4)_3\text{-LiBH}_4$ 1:1.

We have determined the novel eutectic composition $x\text{LiBH}_4 - 1-x\text{KBH}_4$ ($x = 0.7 - 0.75$) ($T_{\text{melt}} \sim 105$ °C), which has the lowest melting point of all alkali and alkaline earth metal borohydride mixtures.² The correct eutectic composition has been found using *in situ* SR-PXD, DSC and temperature programmed photographic analysis. Crystalline KBH_4 is observed by *in situ* SR-PXD after melting of a KBH_4 rich sample with an incorrect ratio of the eutectic mixture, while DSC records the polymorphic transition for LiBH_4 in a LiBH_4 rich sample. Mechanochemistry and manual mixing of LiBH_4 and KBH_4 facilitate the formation of $\text{LiK}(\text{BH}_4)_2$ from $\text{LiBH}_4 - \text{KBH}_4$ 1:1.³ *In situ* SR-PXD reveals that the bimetallic borohydride $\text{LiK}(\text{BH}_4)_2$ disassociates at 90 °C into LiBH_4 and KBH_4 followed by incomplete melting at 105 °C. The solidification process of the eutectic mixture has also been studied by *in situ* SR-PXD.

Composite samples of $\text{Y}(\text{BH}_4)_3\text{-LiBH}_4$ 1:1 and $\text{Y}(\text{BH}_4)_3\text{-LiCl}$ 1:1 have been prepared from halide-free $\text{Y}(\text{BH}_4)_3$ obtained from the novel solvate $\text{Y}(\text{BH}_4)_3\text{S}(\text{CH}_3)_2$.⁴ Melting occurs in the composite samples at ~ 190 °C. The samples are considerably destabilised by the melting event, which facilitates release of hydrogen immediately after melting. The structure of $\text{Y}(\text{BH}_4)_3\text{S}(\text{CH}_3)_2$ has been solved from powder diffraction data. $\text{Y}(\text{BH}_4)_3\text{S}(\text{CH}_3)_2$ consists of buckled layers of slightly distorted octahedrons of yttrium atoms coordinated to five borohydride groups and one dimethyl sulphide group. The buckled layers are interconnected by weak $\text{C-H} \cdots \delta^-\text{H-B}$ interactions between CH_3 and terminal BH_4 groups, with partial positive and negative charges on hydrogen.

[1] Paskevicius, M. *et al.*, *PCCP*, 2013, 15, 19774. [2] Ley, M. B., Roedern, E. & Jensen, T. R., *in preparation*, 2014. [3] Nickels, E. A. *et al.*, *Angew. Chem. Int. Ed.*, 2008, 47, 2817. [4] Ley, M. B., Schouwink P. *et al.*, *in preparation*, 2014.

Keywords: Powder diffraction, Metal borohydrides, Hydrogen storage, Eutectic

Application of time-resolved *in situ* synchrotron X-ray powder diffraction in the study of non-equilibrium phase transformation of LiFePO₄ during high rate electrochemical cycling

Hao Liu^a, Fiona C. Strobridge^a, Olaf J. Borkiewicz^b, Kamila M. Wiaderek^b, Karena W. Chapman^b, Peter J. Chupas^b & Clare P. Grey^{a,c*}

^a Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge CB2 1EW, UK

^b X-ray Science Division, Advanced Photon Source, Argonne National Laboratory, Illinois 60439, USA

^c Department of Chemistry, Stony Brook University, New York 11794-3400, USA

email: cpg27@cam.ac.uk

A fundamental understanding of an electrode material requires the elucidation of its phase transformation mechanism during charge and discharge. *Ex situ* methods, which are carried out under equilibrium condition, have been widely used in characterizing the thermodynamic phases at different states of charge, from which a thermodynamic phase transformation pathway can be constructed. However, *ex situ* measurements do not always reflect the process occurred in an operating battery as the non-equilibrium operating condition might result in deviations from the thermodynamic process, especially for high-rate materials, such as LiFePO₄, which is predicted to exhibit a fundamentally different phase transformation process at high rates^{1,2}. To probe the process at high rate, an *in situ* method with reasonable temporal resolution must be employed. In this work, the high rate galvanostatic cycling process of LiFePO₄ nanoparticle electrode in a customised AMPIX cell³ was investigated *in situ* by time-resolved synchrotron X-ray powder diffraction. Formation of continuous non-equilibrium solid solution phases between LiFePO₄ and FePO₄ was observed at 10 C rate. The *in situ* diffraction patterns were analysed by a refinement strategy that accounts for the asymmetrical diffraction peak profiles due to Li composition variations.

[1] P. Bai, D. A. Cogswell, and M. Z. Bazant, *Nano Lett.*, 2011, 11, 4890–4896.

[2] R. Malik, F. Zhou, and G. Ceder, *Nat. Mater.*, 2011, 10, 587-590.

[3] O. J. Borkiewicz, Badri Shyam, Kamila M. Wiaderek, Charles Kurtz, Peter J. Chupas, and Karena W. Chapman, *J. Appl. Crystallogr.*, 2012, 45, 1261–1269.

Keywords: *in situ*, Li-ion batteries, phase transition, solid solution, peak asymmetry

Operando XRD-DRIFTS investigation during Fischer-Tropsch synthesis over cobalt supported catalysts: Influence of crystalline structure

Virginie Moizan^a, J. Scalbert^a, I. Cléménçon^a, C. Legens^a, F. Diehl^a, D. Decottignies^a, S. Maury^a & A. Fécant^a

^aIFP Energies nouvelles, Solaize, France, e-mail: virginie.moizan@ifpen.fr

Fischer-Tropsch (FT) synthesis over cobalt-based catalysts can potentially contribute to the diversification of fuel sources, as a path to convert natural gas, coal or biomass into liquid hydrocarbons of high purity. However, reaction mechanisms and deactivation pathways are still unclear and subjects to various studies and discussion [1-2].

The aim of the study was to investigate the crystalline structure and the surface of model cobalt-based catalysts during the Fischer-Tropsch synthesis by the means of an innovative operando tool developed at IFPEN combining an X-Ray Powder Diffractometer (XRPD), a Diffuse Reflectance Infrared Fourier Transform (DRIFT) spectrometer and an original environmental cell [3-4].

Several cobalt-based catalysts reduced *in situ* under various conditions and their crystalline structure was monitored using the operando XRD methodology. The catalytic performances were then evaluated under realistic FT synthesis conditions, with various temperatures, pressures (up to 18 bar) and H₂/CO ratio. The crystalline structure of the catalysts was observed by the means of XRD, while the surface of these catalysts was investigated using DRIFT spectroscopy. An online gas chromatography allowed the characterization of H₂, CO and gaseous reaction products.

Crystalline structure, oriented during the activation step, was found to have a strong impact on the catalytic properties. XRD and DRIFTS characterizations during the reaction allowed to support or understate some possible mechanisms and, for the first time at our knowledge, to propose clear correlations between the catalyst structure and surface and its catalytic properties. A surface reconstruction phenomenon was highlighted at the early stages of the reaction, and the formation of heavy unsaturated and oxygenated hydrocarbons was suggested to be a major cause of deactivation.

[1] O. Ducreux, B. Rebours, J. Lynch, M. Roy-Auberger, D. Bazin, *Oil & Gas Science and Technology* 2009, 64,49. [2] H. Karaca, O.V.

Safonova, S. Chambrey, P. Fongarland, P. Roussel, A. Griboval-Constant, M. Lacroix, A.Y. Khodakov, *Journal of Catalysis* 2011, 277, 14. [3] L. Braconnier, I. Cléménçon, C. Legens, V. Moizan, F. Diehl, H. Pilliere, P. Echegut, D. De Sousa Meneses, Y. Schuurman, *Journal of Applied Crystallography* 2013, 46, 262. [4] L. Braconnier, E. Landrison, I. Cléménçon, C. Legens, F. Diehl, Y. Schuurman, *Catalysis Today* 2013, 215, 18.

Keywords: Operando analysis, XRPD, DRIFT spectroscopy, Fischer-Tropsch

MS08_P97

Formation, Growth and Phase Transition of Colloidal Monodisperse Spherical Copper Sulphide Nanocrystals: An *In Situ* XRD Study

Peter Nørby^a, Simon Johnsen^a & Bo Brummerstedt Iversen^a

^aCenter for Materials Crystallography, Department of Chemistry and iNANO, Aarhus University, e-mail: noerby@chem.au.dk

The physical and chemical properties of colloidal metal chalcogenide semiconductor nanocrystals can be modified by minor changes of the morphology, size and/or crystal phase [1]. Although, colloidal copper sulphide nanocrystals, have been used in e.g. solar cells [2], they have not been studied as comprehensively as the lead and cadmium analogues. For progress in the development of customised colloidal copper nanocrystals, understanding the mechanisms controlling formation and growth during synthesis is of key importance.

We have used *in situ* synchrotron powder X-ray diffraction (PXR) to study the formation, growth, and phase transition of colloidal monodisperse spherical copper sulphide nanocrystals synthesised in dodecanethiol. Recently, we have shown that *in situ* PXR provides unique information about how to control the size and phase of nanoparticles as a function of time and temperature [3]. In the present study, we found that the crystalline precursor [CuSC₁₂H₂₅] decomposes upon heating and forms an isotropic liquid that subsequently turns into colloidal β -chalcocite phase Cu₂S nanocrystals. Further heating results in a solid state rearrangement phase transition of the β -chalcocite phase nanocrystals to high digenite phase nanocrystals. We show by *in situ* PXR and TEM how the nanocrystal size and phase of colloidal monodisperse copper sulphide nanocrystals varies as a function of synthesis temperature and time.

[1] Burda, C.; Chen, X. B.; Narayanan, R.; El-Sayed, M. A., *Chem. Rev.* 2005, 105, 1025 [2] Wu, Y.; Wadia, C.; Ma, W.; Sadtler, B.; Alivisatos, A. P., *Nano Lett.* 2008, 8, 2551 [3] Nørby, P.; Jensen, K.

M. Ø.; Lock, N.; Christensen, M.; Iversen, B. B., *RSC Adv.* 2013, 3, 15368

Keywords: Colloidal Nanocrystals, *In Situ* X-ray Diffraction, Copper Sulphide, Phase Transition, Crystal Growth

MS08_P98

Maghemite nanoparticle formation under the influence of mussel-inspired additives

Vicki Nue, Haraldur P. Gunnlaugson & Henrik Birkedal

University of Aarhus, Denmark, e-mail: vnue@chem.au.dk

Iron(III) oxide nanoparticles are of interest for several applications, e.g. as magnetic resonance imaging contrast agents. The magnetic properties of nanoparticles depend strongly on their size. To control nanoparticle size it is important to understand the crystallization kinetics. This can be achieved using e.g. *in situ* X-ray diffraction^{1,2}. Herein, a mussel-inspired synthesis of maghemite (Fe₂O₃) nanoparticles was developed. The kinetics of nanocrystal formation were studied using *in situ* X-ray diffraction.

Nanoparticle growth can be controlled by additives^{1,2}. The blue mussel utilizes the catechol-containing DOPA to adhere to inorganic surfaces via coordination bonds to the catechol. These bonds are also used in self-healing coatings of the mussel beard³. This chemistry has been harnessed in synthetic hydrogel systems^{4,5}. The strong Fe(III) catechol bond makes the catechol suitable for controlling the formation of iron(III) oxide nanoparticles. Herein, we used dopamine or hydrocaffeic acid as additive leading to, respectively, amine or carboxylate functionalized nanoparticles.

A Fe(II)/Fe(III) solution containing the organic additive was added drop wise to a warm base⁶. For the *in situ* experiment a flow cell with high temperature stability was utilized². The flow prevents sedimentation during the reaction. *In situ* X-ray diffraction studies were performed at MAXLAB using a CCD detector.

Rietveld refinement of *ex situ* diffraction data show that the maghemite particles are octahedrons in shape. *In situ* X-ray diffraction showed that nucleation happens almost instantaneously upon addition of the iron-containing solution. The crystalline phase co-exists with an amorphous phase that most likely is a highly disordered ferrihydrite. The ratio between the amorphous and crystalline phase is dependent on the additive.

The present synthesis provides a new route to magnetic nanoparticles with controlled size. Detailed analysis of reaction kinetics by in situ X-ray diffraction sheds light on nanoparticle formation that will be useful for the development of improved/modified syntheses.

[1] C. J. S. Ibsen and H. Birkedal, *Nanoscale*, 2010, 2, 2478-2486. [2] C. J. S. Ibsen and H. Birkedal, *J. Appl. Cryst.*, 2012, 45, 976-981. [3] N. Holten-Andersen et al, *Nature Materials*, 2007, 6, 669-672. [4] N. Holten-Andersen et al, *PNAS*, 2011, 108, 2651-2655. [5] M. Krogsgaard et al, *Biomacromolecules*, 2013, 14, 297-301. [6] E. K. U. Larsen et al, *ACS Nano*, 2009, 3, 1947-1951.

Keywords: In situ, Bioinspired, Magnetic nanoparticles, Nanocrystals, Crystal growth

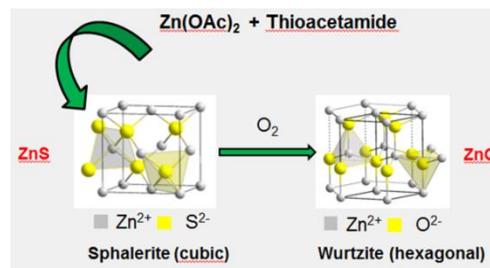


Fig. 1: overview of investigated reactions

[1] Lu, H.-Y.; Chu, S.-Y.; Tan, S.-S., *Journal of Crystal Growth*. 2004, 269, 385-391

Keywords: in-situ XRD, nanoparticles, crystallite growth

MS08_P99

Investigation of Synthesis Parameters on Growth of Semiconducting Nanoparticles

Andreas Pein^a & Christian Resch^a

^a Anton Paar GmbH, Austria, andreas.pein@anton-paar.com

Nanoparticles have attracted considerable interest in recent times. This can be mainly attributed to their tuneable, size-dependent optical and optoelectronic properties.

Especially semiconducting nanoparticles are highly researched materials because of the wide field of possible applications, like solar cells, infrared windows, lasers and displays. Zinc sulphide (ZnS) and zinc oxide (ZnO), both belonging to the group of II-IV semiconductors, with band gap energies of 3.66 and 3.2 eV are among the most prominent candidates. Although these materials are well-known, there is still a need to find a fast and cost-effective synthesis procedure.

This contribution describes an already established solid-state synthesis method of ZnS nanoparticles, using zincacetate (Zn(OAc)₂) and thioacetamid (TAA) as precursors.^[1] These particles can be easily oxidized to ZnO nanoparticles by applying a temperature of 600°C in air. (see Fig. 1)

The synthesis method is studied by in-situ XRD characterization, performed with the XRK 900 Reactor Chamber of Anton Paar. Additional information about the influence of temperature, temperature ramp and waiting time on the size of resulting crystallites is obtained. Also the time for a complete oxidation to ZnO nanoparticles is investigated.

MS08_P100

Evolution of microstructure and local structure of Li-rich layered oxides Li_{1+x}M_{1-x}O₂ during cycling: their effect on the redox mechanisms occurring upon battery operation

Alexandre Pradon^a, Camille La Fontaine^b, Stéphanie Belin^b, Erik Elkaïm^b, Pierre-Emmanuel Petit^a, Rémi Dedryvère^c, Erwan Dumont^d, Luc Lajaunie^a, Philippe Moreau^a, Cécile Tessier^d, Guy Ouvrard^a & Maria Teresa Caldes^a

^aInstitut des Matériaux Jean Rouxel (IMN), Université de Nantes, CNRS, 2 rue de la Houssinière BP 32229, 44322 Nantes Cedex 3, France;

^bSynchrotron SOLEIL, l'Orme des Merisiers, Saint-Aubin BP48, 91192 Gif-sur-Yvette cedex;

^cIPREM-ECP (UMR 5254 CNRS), University of Pau, 64053 Pau Cedex 9, France;

^dSaft, 111 boulevard Alfred Daney, 33074 Bordeaux Cedex, France
e-mail: pierre-emmanuel.petit@cnrs-imm.fr

Li-rich layered oxides Li_{1+x}M_{1-x}O₂ with M = Mn, Co and Ni are high-potential materials to be used as positive electrode in Li-ion batteries. These materials can be described as an intergrowth between [LiO₆]_∞ and [MO₆]_∞ octahedral layers. Over-lithiation induces a Li₂MnO₃-type order into [MO₆]_∞ slabs which facilitates oxygen ions oxidation at high potential (>4.4 V), a phenomenon responsible for the extra-capacity observed in these Li-excess compounds compared to stoichiometric ones (300 mAh/g vs 200 mAh/g). Although their average structure is well-known nowadays [1-2], the local structure and microstructure need further investigations, as they can affect notably Li ion transport.

In this work two electrodes with different starting microstructures both activated up to 4.6 V at different temperatures have been studied. To follow the structural

and redox changes under battery operation (*operando* mode), we performed at synchrotron SOLEIL both x-ray diffraction (XRD) and x-ray absorption spectroscopy (XAS; Mn, Co and Ni K-edges) experiments. In addition to XRD results, the evolution of microstructure (bulk and surface) during cycling was also monitored in *ex-situ* mode by high resolution transmission electron microscopy (HREM) and x-ray photoelectron spectroscopy (XPS; O K and Mn L₂/L₃ edges).

During charge a progressive alteration of the Li₂MnO₃-type order occurs at high potential. Many stacking faults are observed by HREM, especially at high activation temperature. In addition, spinel-type defects are visible at the crystals boundaries that are probably at the origin of the voltage decrease observed during cycling. The formation of spinel-type defects is compatible with the surface enrichment in manganese, as evidenced by XPS. While the activation temperature has an influence on XAS spectra obtained at Co and Ni K-edge, the influence of the microstructure is only noticeable at Mn K-edge.

[1] H. Koga et al., Journal of the Electrochemical Society, 2013, A1, 160 [2] H. Yu et al., The Journal of Physical Chemistry Letters, 2013, 4, 1268

Keywords: Li-ion batteries, layered oxides, XRD, XAS, *operando* mode

MS08_P101

Operando studies of electrochemically driven phase transitions in nanoscale olivine cathodes for Li-ion batteries

Dorthe B. Ravnsbæk^{a,b}, Kai Xiang^a, Wenting Xing^a, Olaf Borkiewicz^c, Kamila Wiaderek^c, Peter Chupas^c, Karena Chapman^c & Yet-Ming Chiang^a

^aDepartment of Material Science and Engineering, MIT, 02139 Cambridge, MA, USA (dorthe@mit.edu)

^biNANO, Aarhus University, 8000 Aarhus, Denmark

^cAdvanced Photon Source, Argonne National Laboratory, 60439 Argonne, IL, USA

Compounds of interest for ion storage in advanced batteries frequently exhibit phase transformations, driven by large and variable electrochemical driving forces inherent to practical use. Understanding how materials variables (e.g. composition and nanoscale-crystallite) affect the phase transition is of vital importance for practical applications as the reversibility and stability of these structural transformations determine the energy, power, and lifetime of the system. Furthermore, the dynamic electrochemical conditions

relevant for practical battery operation are often far from equilibrium. Therefore, it is of high importance to investigate these changes by *operando* techniques.

Due to its outstanding power, safety and cycle-life olivine LiFePO₄ (LFP) has during the past decade become a widely used, and is today one of the most well-studied, lithium ion battery cathode materials. It is well-established that for LFP the storage/release of lithium is accompanied by a first-order phase transition between lithiated and delithiated states. However, it would be a mistake to conclude that the behavior of pure LFP is representative of all olivines.^{1,2}

Utilizing *operando* synchrotron radiation powder X-ray diffraction (SR-PXD), we demonstrate here, by systematic screening of the electrochemical driven phase transitions in a series of LiMn_yFe_{1-y}PO₄ (y = 0.1-0.8) powders, a completely different phase transformation mode dominated by formation of metastable solid solutions for nanoscale LiMn_yFe_{1-y}PO₄ compared to the binary lithiation states within the extremely well-studied case of LFP.³ Rietveld refinement reveals small elastic misfits strains between phases within the extended solid solution regime. On the basis of the time- and state-of-charge dependence of the olivine structure parameters, we propose a coherent transformation mechanism, and finally, we bring evidence that the observed metastability is enabled by particle size reduction to the nanoscale.

This work was supported by DOE project number DE-SC0002626. Work at APS was supported by DOE Contract No.DE-AC02-06CH11357. D.B.R. acknowledges the Carlsberg Foundation for funding.

[1] Meethong et al. *Adv. Funct. Mater.* **2009**,19,1060 [2] Chung et al. *Nat. Mater.* **2002**,1,123. [3] Ravnsbæk et al. *Nano Lett.* 2014 DOI.

Keywords: Battery cathodes, phase transformation

MS08_P102

Water retention mechanism in the case of Hg exchanged montmorillonite: Structural characterization

Marwa Ammar^a, Walid Oueslati^b, Abdesslem Ben Haj Amara^a & Hafsia Ben Rhaïem^a

^aUR 05/13-01 : Physique des Matériaux Lamellaires et Nanomatériaux Hybrides (PMLNMH), Faculté des Sciences de Bizerte, Zarzouna 7021, Tunisia.

^bTechnical and Vocational Training Corporation; College of Electronics & Communications, General studies department, TV street, P.O.Box 2816 Jeddah 21461, Kingdom Of Saudi Arabia.
e-mail: walidoueslati@ymail.com

This work focuses the effect of hydration dehydration cycles orientation, produced in situ using a continuous variation of relative humidity (%RH) rate, on the water retention mechanism for Hg exchanged montmorillonite (i.e. SWy-2-Hg). This aim is achieved using the quantitative XRD analysis based on the modeling approach which consists in the comparison of experimental 00l reflections with the calculated ones deduced from structural models. This approach allows us to determine the amount of the interlayer water molecules, structural changes along the c^* axis and reaches the relative layer types contributions. The obtained main results show that all experimental profiles are simulated using a mixed layer structure with various proportions of bihydrated (0W), mono-hydrated (1W), dehydrated (2W) and three- hydrated (3W) layer types, which demonstrate the heterogeneous hydration character over all %RH rates. The obtained response for this hydrous perturbation is accompanied by an irreversible gradual growth of the interlayer water molecules content.

Keywords: Hg exchanged montmorillonite, hydration-dehydration cycle, Mixed Layer Structure, interlayer water.

powder data of the anti-fluorite structure type Ag_2Te [1]. A Li superionic phase transition was found from analysis of neutron powder data of Li_2Te [2].

Here we present a detailed adp-analysis of neutron powder data up to 271°C of the Zintl-phase compound NaTl, using the Rietveld program JANA2006 [3].

The quasi-harmonic (linear) temperature dependence of harmonic Na adp's shows a distinct steepening of slope around 200°C, indicating a transition to a superionic phase. Pdf's, atom potentials and atom restoring forces modeled by anharmonic adp-analysis will be compared to those derived from harmonic split atom models. The results clearly demonstrate the smearing out of pdf's within the Na sublattice above the superionic phase transition. The corresponding softening of Na-potentials mark the transition to Na-sublattice melting, which is complemented by a decrease of Na site occupancies and a "liquid like" modulation of the background.

[1] Schneider J., Schulz H., Z. Kristallogr. 1993, **203**, 1-15

[2] Schneider J., Schröder T., Hölzel M., Oeckler O., Schmahl W.W., 21st Annual Conf. of the German Crystallographic Soc., 2013, Freiburg, Germany

[3] Petricek V., Dusek M., Palatinus L. : JANA2006

Keywords: neutron powder diffraction, adp-analysis, superionic phase transition

MS08_P103

From Powders to Potentials: Cation sublattice melting in NaTl

[Julius Schneider](#) & [Wolfgang W. Schmahl](#)

Ludwig-Maximilians-Universität München Department of Earth- and Environmental Sciences Crystallography Section, Theresienstr. 41, D-80333 München, Germany, juschneider@kabelmail.de

Standard analysis of powder diagrams yields information on crystal structures in terms of the average (static) position of atoms. In addition, a wealth of information on the dynamics of crystal structures may be gained from the analysis of atom displacement factors (adp's).

In the harmonic approximation spherical or elliptical vibration amplitudes of atoms are assumed, depending on their respective site symmetries. A generalization towards higher order potentials often reveals dynamic anomalies of atoms, in particular in the vicinity of phase transitions.

Calculation of the Fourier transform of adp's yields 3-D probability density functions (pdf's), atom potentials and atom restoring forces.

An early demonstration showed the temperature variation of joint Ag atom pdf's derived from X-ray

Kinetics of stress-induced phase transformation in superelastic NiTi: an in-situ X-ray diffraction study

[Nikolay Zotov](#)^a, [Efthymios Polatidis](#)^a, [Peter Wochner](#)^b & [Eric J. Mittemeijer](#)^{a,c}

^aMax Planck Institute for Intelligent Systems, Stuttgart, Germany, email: n.zotov@is.mpg.de

^bMax Planck Institute for Solid State Research, Stuttgart, Germany

^cInstitute for Material Science, University of Stuttgart, Stuttgart, Germany

Superelastic NiTi alloys exhibit a reversible austenite-martensite phase transformation under tension, compression and/or torsion¹. Knowledge of the evolution of the martensite fraction with loading/unloading is important not only for understanding the nature of the transformation but it could also aid practical applications. In-situ X-ray diffraction was performed to study the nucleation of martensite, the propagation of the austenite-martensite interfaces and the evolution of the microstructure during uniaxial tensile loading under elongation control with 0.1 mm/s. The in-situ diffraction experiments were performed both with a laboratory Bruker D8 diffractometer equipped with a SOLIX solid state detector as well as with synchrotron radiation using a 2D MarCCD detector on the MPI beamline at ANKA, Karlsruhe. It is shown that the nature of the transformation (localized versus uniform) and the amount of retained austenite depend on the thermo-mechanical history (annealing, thermal cycling, mechanical cycling etc.). On the other hand, the overall kinetics of the transformation (evolution of the martensite fraction) is less sensitive to the thermo-mechanical treatment and the amount transformed is approximately linear as a function of the applied strain. Analysis of the broadening of the austenite diffraction peaks indicates the presence of austenite grain populations with different crystallite sizes and microstrains, whereas analysis of the peak shifts indicates that the austenite phase experiences different macrostresses during loading/unloading along the strain gauge.

[1] K. Otsuka and C.M. Wayman, Shape Memory Materials. Cambridge University Press, London, 1998.

Keywords: NiTi, superelastic, tensile tests, in-situ XRD, austenite-martensite transformation, kinetics

*Microsymposium MS09:
Nanomaterials, surfaces and interfaces*

*Chairs: Matteo Leoni, University of Trento (IT)
Nina Lock, Aarhus University (DK)*

*Microsymposium: Wednesday 18 June 2014 Morning – Chemistry AUD I, 1514-213
Poster session: Monday 16 June 2014 – iNANO building, 1593-012*

MS09_K1

High-energy surface X-ray diffraction applied to model catalysis

Johan Gustafson^a

^aLund University, Sweden, e-mail: johan.gustafson@sljus.lu.se

Surface X-ray diffraction (SXRD) is one of few methods available for surface structure determination under ambient conditions. Using conventional SXRD, however, exploring 2D maps from a substantial part of reciprocal space is extremely time-consuming, and mapping of the 3D reciprocal space with high resolution is currently impossible even with synchrotron radiation. As a result, the probed surface structure has to be known qualitatively from other measurements, and an unexpected structure may easily be left unnoticed, especially under harsh conditions.

In this contribution I will demonstrate how the use of high-energy X-rays (85 keV) in combination with a large 2D detector accelerates the data collection by several orders of magnitude and enables full surface-structure determination by 3D mapping of reciprocal space on a time scale suitable for in situ studies [1]. In addition, the small diffraction angles, resulting from the high photon energy, and the large detector result in data that are easily presented in a more intuitive way, since each detector image contains the projection of a full plane in reciprocal space and straight lines in reciprocal space correspond to straight lines on the detector.

We have used this method to analyse the structure of an ultra-thin surface oxide formed on Rh(111) during high CO oxidation activity. Especially, we find that the structure differs slightly from that formed in pure O₂. Although the difference is small, it might have large implications for the understanding of the catalytic CO oxidation over Rh.

[1] J. Gustafson, M. Shipilin, C. Zhang, A. Stierle, U. Hejral, U. Ruett, O. Gutowski, P.-A. Carlsson, M. Skoglundh, and E. Lundgren, *Science* 2014, 343, 758

Keywords: high-energy surface X-ray diffraction, catalysis, Rhodium oxide

X-ray imaging of single nano-crystals

Vincent Favre-Nicolin^{a,b}, Marta Elzo Aizarna^{a,b}, Ondrej Mandula^{a,c}, Francesca Mastropietro^{a,d,e}, Joël Eymery^a, Gerardina Carbone^d, François Andrieu^f, Odile Robach^a, Julien Claudon^a & Jean-Michel Gérard^a

^aCEA-UJF, INAC, SP2M, Grenoble, France,

^bUniv Grenoble Alpes, France,

^cFondation Nanosciences, Grenoble, France,

^dEuropean Synchrotron Radiation Facility, France

^eUniversité Aix-Marseille, Institut Fresnel, France

^fCEA-LETI, Minatec, Grenoble, France

e-mail: vincent.favre-nicolin@cea.fr

The last two decades have seen a fast development of sub-micrometric crystalline structures, in order to yield new properties through quantum confinement, to achieve further miniaturization or to enhance the energetic efficiency of nano-devices. This has been particularly important for semi-conductor nano-structures for photonic and electronic applications, as well as for nano-electro-mechanical systems.

In the same timeframe, experimental methods for structural determination at the nanoscale have also been developed, using mostly electron microscopy and X-ray scattering. In this presentation, we will focus on the use of X-ray nano-beams: thanks to efficient focusing optics, it is now possible to produce coherent and intense X-rays ($>10^5$ ph/s/nm² monochromatic) with small lateral sizes (<100 nm) on synchrotron beamlines. These nano-beams can be used to perform different types of experiments: Coherent Diffraction Imaging (CDI) and Ptychography can be used to recover the shape and (in Bragg geometry) the deformation map of individual nano-structures. Using a white beam, micro-Laue diffraction can be used to recover the local structure and deformation of a crystal using single-shot images.

In this presentation we will discuss the advances of these different techniques, their advantages compared to the analysis of ensemble-averaged methods, and show results obtained on semiconductor nano-structures for photonic and electronic applications.

[1] Miao J, Charalambous P, Kirz J & Sayre D, *Nature*, 1999, 400, 342 [2] Newton MC, Leake SC, Harder R & Robinson IK, *Nat Mater*, 2010, 9, 120 [3] Favre-Nicolin V, Eymery J, Koester R & Gentile P, *Phys Rev B*, 2009, 79, 195401 [4] Favre-Nicolin V, Mastropietro F, Eymery J, *New J Phys*, 2010, 12, 35013. [5] Tamura N, MacDowell A A, Spolenak R, Valek B C, Bravman J C, Brown W L, Celestre R S, Padmore H A, Batterman B W and Patel J R, *Journal of Synchrotron Radiation*, 2003, 10, 137–43 [6] Ulrich O, Biquard X, Bleuet P, Geaymond O, Gergaud P, Micha J S, Robach O and Rieutord F, *Rev. Sci. Instrum.*, 2011, 82, 033908 [6] F. Mastropietro, J. Eymery, G. Carbone, S. Baudot, F. Andrieu, and V. Favre-Nicolin *Phys. Rev. Lett.* 2013, 111, 215502

Keywords: nanostructures, coherent diffraction imaging, X-ray microdiffraction

MS09_O1

Nanocrystalline powder diffraction as a surface science tool.

Zbigniew Kaszku^a

^aInstitute of Physical Chemistry, Polish Academy of Sciences, Poland, e-mail: Zkaszku@ichf.edu.pl

Atoms at a surface of nanocrystals contribute appreciably to the x-ray diffraction pattern. Phenomena like chemisorption, affecting surface atoms displacement in respect to positions in the perfect crystal lattice cause diffraction peaks shift and their intensity changes. Those effects are well measurable for small nanocrystals up to 10 nm size. The diffraction effects of chemisorption of adsorbing gases- H₂, O₂, CO and NO are followed for nanocrystalline Pt supported on silica. A time resolved observation of surface reconstruction on hydrogen desorption [1] allows scaling of its diffraction effects with an average crystal size. This, together with atomistic simulations enabled quantitative diffraction patterns analysis and a way to detect a high pressure surface reconstruction in difference to the relaxation effects. Although Pt nanocrystal bare surface reconstructs spontaneously some adsorbates lift this reconstruction and some (CO, NO) cause deeper reconstruction under atmospheric pressure. For NO at moderate temperatures (80°C) observed is [2] a quick coalescence of Pt nanocrystals-phenomenon known for temperatures above 600°C. This low temperature coalescence is clearly correlated with reconstruction phenomena and the postulated mechanism is via self lifting cyclic surface reconstruction driving cluster transport and crystallization.

The proposed powder diffraction in situ technique together with mass spectrometry turns out to be a unique tool offering insight into structure of reacting nanocrystal surface and in particular enables detection of a high pressure surface reconstruction.

[1] P.Rzeszotarski, Z.Kaszku, Phys.Chem.Chem.Phys. 2009, 11, 541
[2] Z.Kaszku, B.Mierzwa, W.Juszczuk, P.Rzeszotarski, D.Lomot, RSC Advances, 2014, DOI:10.1039/C3RA48078J.

Keywords: in situ diffraction, time-resolved diffraction, nanocrystals, atomistic simulations

Novel method for solving and refining the structure of thin film phases using Cu x-ray radiation and 2D detectors.

Carlos Frontera^a, Xavier Marti^{b,c}, Anna Crespi^a & Jordi Rius^a

^aInstitut de Ciència de Materials de Barcelona, CISC, Bellaterra, Spain, e-mail: frontera@icmab.es

^bInstitut Català de Nanotecnologia, Bellaterra, Spain

^cInstitut of Physics ASCR, v.v.i. Cukrovarnická, Prague, Czech Republic.

We present a combined experimental and computational method which enables the precise determination of the atomic positions in a thin film using Cu radiation only. The capabilities of this technique surpass simple structure refinement and even allow for the resolution of unknown phases stabilized by substrate-induced stress. We derive the appropriate corrections to transform the measured integrated intensities into structure factors. The data collection was performed entirely using routinely available Cu-tube-based diffractometers, and the subsequent analysis utilises single crystal direct methods and/or unit cell refinement by least square procedure. We selected an epitaxial thin film of CuMnAs grown on top of a GaAs substrate, which formed a crystal structure with tetragonal symmetry, differing from the bulk material which is orthorhombic. Here we demonstrate the new tetragonal form of CuMnAs obtained on GaAs substrates and present consistent high-resolution scanning transmission electron microscopy and stoichiometry analyses [1].

The method has been proved to be very useful and we have successfully applied it to different thin film oxides. The refinement of the structure has been able to provide confident information of bond distances and bond angles in different systems and even in a film of only 10 nm thick [2].

[1] P. Wadley *et al.* J. Appl. Cryst., **46**, 1749 (2013).

[2] R. Serrao *et al.* Phys. Rev. B **87**, 085121 (2013)

Keywords: Thin films, epitaxial, structure factor determination, laboratory x-rays.

Modelling the diffraction pattern of faulted nanocrystals

Robert Koch^a & Matteo Leoni^a

^aUniversity of Trento, Trento, 38123, Italy, e-mail: Robert.Koch@unitn.it

Matteo.Leoni@unitn.it

The Debye scattering function (DSF) is usually regarded as the only solution to model the diffraction pattern of heavily faulted structures, as a traditional Rietveld refinement fails in reproducing the experimental evidence [1]. Unfortunately, the DSF can be severely limited by computational overhead, especially when layer faulting is analyzed from powder diffraction data. In these situations, the computational cost associated with building enough patterns to achieve a good grain ensemble average is often prohibitive. With such extensive disorder, a fast reciprocal space approach, such as e.g. the Rietveld method [2] or the Whole Powder Pattern Modelling (WPPM [3]), would be desirable. Those methods, however, are typically based on a 3D periodic lattice, and thus they cannot (easily) deal with diffuse scattering features or with non-crystallographic systems. Additionally, many of the traditional techniques or implementations fail to consider microstructure in a physically meaningful way. We present here the application of a fast Rietveld-like Fourier formalism that can consider physical instrumental and microstructure effects and reproduce the patterns of any structure showing 2D to 3D periodicity, with the accuracy typical of the DSF. Examples are shown, where the technique is compared to DSF data from ensembles of faulted nickel nanocrystals.

We demonstrate that structural and microstructural parameters describing the crystal ensemble, including details on the fault quantity as well as crystal shape and size distribution, can be recovered through non-linear least squares fitting of the simulated data.

[1] P. Scardi, M. Leoni, K. R. Beyerlein, *Z. Kristall.* 2011, 226, 924–93

[2] R. A. Young, Ed., Oxford University Press, 1995

[3] P. Scardi, M. Leoni, *Acta Crystall. A* 2002, 58, 190–200

Keywords: XRD, Stacking faults, crystal size effects

Unravelling the growth of Pt nanorods inside a porous matrix by Debye Function Analysis

Antonietta Guagliardi^a, Ruggero Frison^a, Antonio Cervellino^b, Cernuto Giuseppe^c, Angelo Maspero^c, Mohammad Hayatifar^d, Stefano Zacchini^d & Norberto Masciocchi^c

^aIstituto di Cristallografia, CNR, I-22100 Como, Italy

^bPaul Scherrer Institut, CH-5232 Villigen, Switzerland

^cDipartimento di Scienza e Alta Tecnologia, Università dell'Insubria, I-22100 Como, Italy.

^dDipartimento di Chimica Industriale, Università di Bologna, I-40136 Bologna, Italy.

e-mail: antonella.guagliardi@ic.cnr.it

Careful control of the size and shape of noble metal nanoparticles allows their (catalytic, electronic, magnetic) properties to be modified and their applications tuned in many fields of interest.^[1] However, strictly controlling these microstructural properties in elongated nanoparticles (nanorods and nanowires) remains a key issue within the *bottom-up* approach to Nanoscience, since conventional solution, colloidal and vapour phase synthetic methods rarely lead to monodisperse materials. On the other side, nanoporous (either amorphous or crystalline) matrices offer the advantage of a size/shape selectivity originating from the geometrical constraint of their pores/channels, making their use as nano-reactors rather appealing.^[2]

Amorphous silica of MCM-41 type and metal-organic frameworks (MOFs) with extremely long nitrogen-based ligands were synthesized, both with parallel channels *ca.* 4.0 nm² large; concentrated solutions (20 and 30% in weight) of high-nuclearity Pt carbonyl clusters of the Chini type^[3] (typically, [Pt₁₂(CO)₂₄]²⁻) were, then, used for impregnation to promote (after elimination of the ligand shell) the *in situ* aggregation of largely anisotropic metallic nanoparticles within the confined space of the channels.

The structure and microstructure of the metal NPs were investigated by Debye Function Analysis through the DEBUSSY suite of programs (release 2.0).^[4,5] High resolution synchrotron data were collected at the MS-X04SA@SLS on the pristine supramolecular/hybrid materials and during/after their thermal treatment to induce NPs aggregation within the channels. Pt@SiO₂ samples were obtained after heating the powder at different temperatures from 150 °C up to 300 °C; *in situ* measurements were carried out on Pt@MOF, with T varying from 300 K up to 480 K, ΔT=30 K.

Results will be presented and discussed.

Partial financial support by Fondazione Cariplo (Project No 2011-0289) is acknowledged.

-
- [1] X. Teng, W.-Q. Han, W. Ku, M. Hücker. *Angew. Chem. Int. Ed.*, 2008, 47, 2055.
[2] H.R. Moon, D.-W. Lim, M.P. Suh, *Chem. Soc. Rev.*, 2013, 42, 1807.
[3] I. Ciabatti, C. Femoni, M. C. Iapalucci, G. Longoni, T. Lovato, S. Zacchini. *Inorg. Chem.*, 2013, 52, 4384.
[4] A. Cervellino, C. Giannini, A. Guagliardi. *J. Appl. Cryst.* 2010, 43, 1543.
[5] A. Cervellino, R. Frison, F. Bertolotti, A. Guagliardi, 2014, in *preparation*.

Keywords: Metal Nanorods, Nanoporous Frameworks, Debye Function Analysis

Posters:

MS09_P105

New phases in thin-films of the Zn-Sb system

Anders B. Blichfeld^{a,b} & Bo B. Iversen^a

^a Center for Materials Crystallography, Department of Chemistry and iNANO, Aarhus University, Langelandsgade 140, 8000, Aarhus C, Denmark

^b PhD-stipendiate partly founded by SINO Danish Center for Research and Education

The phase diagram of the intermetallic system of Zn-Sb contains a rich chemistry.[1] Many of the compounds found in the system are of interest for their thermoelectric(TE) properties since they are heavily doped semiconductors. The structure of the compounds varies in complexity from the simple ZnSb to Zn_{38.3}Sb₃ (β -Zn₄Sb₃), both very promising TE materials.[2, 3] One way to improve the efficiency of TE materials are by lowering the thermal conductivity. This can be done by reducing the dimensionality of the materials. The TE properties for β -Zn₄Sb₃ depend immensely on high control of the composition for a given phase.[4] Both properties can be realized in thin-films via PVD methods.

Thin-films with varying Zn and Sb compositions were made with magnetron sputtering. The composition is tuned by varying the composition of the target material and the temperature of the substrate. Depending on the growth parameters new phases are found by X-Ray diffraction(XRD). Subsequent XRD in-situ annealing show that the phases are metastable and develop into the phases found in the bulk phase diagram.

-
- [1] Adjadj, F., E.-d. Belbacha, and M. Bouharkat, *Journal of Alloys and Compounds*, 2007. 430(1-2): p. 85-91.
[2] Snyder, G.J., et al., *Nature Materials*, 2004. 3(7): p. 458-463.
[3] Toberer, E.S., et al., *Journal of Materials Chemistry*, 2010. 20(44): p. 9877-9885.
[4] Dasgupta, T., et al., *Journal of Applied Physics*, 2013. 113(10): p. 103708.

Keywords: Thin-films, ZnSb, β -Zn₄Sb₃

MS09_P106

Solvothermal flow synthesis and PXRD study of the $Pt_{1-x}Ru_x$ system

Martin Bondesgaard^a, Aref Mamakhel^a, Peter Hald^a, Jacob Becker^a & Bo B. Iversen^a

^aUniversity of Aarhus, institute for chemistry, Denmark, e-mail: 20103957@post.au.dk

A synthesis was carried out at different temperatures and stoichiometric compositions for this system and characterized by PXRD. A new extended two phase region at the lower temperature have been found when comparing with the phase diagram for the bulk phase, which is not previous been describe in the literature. For all the different series the crystallite size is presented as a function of temperature. The stoichiometric variation series is present as function of change in the unit cell length when the stoichiometric change for both phases and is following vegard's law.

Keywords: Solvothermal synthesis, nanoparticles, vegard's law, crystallite size, PXRD.

Using mentioned methods the real structure of prepared samples is revealed. The desired parameters are mainly the size and size distribution of nanoparticles and phase composition (including amorphous phase content). Obtained results will be correlated to other investigated properties, for example photo catalytic activity.

- [1] Asahi, R. et al., *Science*, 2001, **293**, 269
- [2] Zhang, L. et al., *Procedia Engineering*, 2012, **27**, 552
- [3] Zhang, L. et al., *Material Res. Bull.*, 2012, **47**, 2188
- [4] Xiao, J. et al., *J. Solid State Chem*, 2006, **179**, 1161
- [5] Zhou, J. et al., *J. Photochem. Photobiol. A*, 2011, **223**, 82

Keywords: real structure, nanopowders, phase analysis, total pattern fitting

MS09_P108

GISAXS studies of mesoporous films using a standard laboratory diffractometer

Milen Gateshki^a, Jan Gertenbach^a, Alexander Kharchenko^a & Patricia Kidd^b

^aPANalytical BV, Almelo, The Netherlands e-mail: jan.gertenbach@PANalytical.com

^bPANalytical Research Centre, SINC University of Sussex, Brighton, United Kingdom

MS09_P107

Structural study of Ce doped TiO₂ nanopowders prepared by super/subcritical fluid extraction

Stanislav Daniš^a, Tereza Brunátová^a, Lenka Matějová^b & Zdeněk Matěj^a

^a Charles University, Faculty of Mathematics and Physics, Dept. of Condensed Matter Physics, Prague, Czech Republic,

^b CNT – Nanotechnology Center, Technical University of Ostrava, Ostrava, Czech Republic

Titanium oxide (TiO₂) is well known material for its photo/catalytic properties under UV-light. However, it was shown that by doping the TiO₂ by cerium, zinc, boron, carbon, noble metal atoms the photo/catalytic activity is enhanced and can be even shifted to visible light region [1-5]. The photocatalytic activity depends not only on doping but on the real crystallographic structure as well.

In our contribution we will present x-ray structure study of cerium doped TiO₂ nanopowders prepared by super/subcritical fluid extraction (H₂O, CO₂) at different temperatures and pressures of the extraction fluid. Conventional x-ray diffraction methods are used (powder diffraction, total pattern fitting procedure).

With the increasing number of GISAXS applications for the investigation of materials surface nano-structures, comes the demand for a mainstream laboratory capability to run alongside the more established synchrotron facilities. GISAXS poses considerable challenges when scaling the method to fit a multipurpose laboratory instrument, including the achievement of good angular resolution at small scattering radius, the reduction of scatter from the direct beam and the observation of low intensity signals. We have developed a hardware solution that addresses these challenges. The recent availability of small size pixel

(55 μm) photon counting detectors with very low noise characteristics has enabled the implementation of new 2D imaging GISAXS hardware for a standard 1.8KW laboratory X-ray source. In this work we present a number of results that illustrate the capabilities of the new experimental set-up based on a standard multipurpose diffractometer. We present GISAXS images and analysis of a mesoporous silica thin film with close-packed hexagonal type ordering of the pores [1]. In earlier work we have reported [2] reflectometry results and analysis of this sample structure. The addition of 2D GISAXS information, obtained on the same type of instrument, demonstrates the versatility of the multipurpose diffractometer and the strength in combining methods on one instrument. Strongly

scattering Ti-filled silica mesoporous films illustrate the relative ease with which GISAXS signals can be recorded, including even the weak signal below the critical angle of the sample. The scattering patterns from both samples exhibit subtle departures from a simple symmetry, suggesting that the films may exhibit residual strain. Thin films with vertical mesopores provide their own challenges in the observation of scatter close and parallel to the specularly reflected beam. We present results in which scattering from Co-filled mesopore structures with 37 nm pitch can be clearly resolved

[1] Samples provided by D. Borah and M.A. Morris, University College Cork, Ireland

[2] R. L. Rice, P. Kidd, J. D. Holmes and M. A. Morris, *J. Mater. Chem.* 2005, 15, 4032

Keywords: X-ray diffraction, grazing incidence small angle scattering, mesoporous materials

MS09_P109

Synthesis and characterization of $\text{Sr}_x\text{Ba}_{1-x}\text{Fe}_{12}\text{O}_{19}$

[Mathilde Gestin^a](#), [Cecilia Granados-Miralles^a](#) & [Mogens Christensen^a](#)

^aCenter for Materials Crystallography, Department of Chemistry and iNANO, Aarhus University, Denmark, e-mail: mathilde.ges@gmail.com

Nowadays, great attention is paid to the study of permanent magnets because they are key components in many applications, like magnetic-recording or electronic devices. Unfortunately the price of rare-earth elements, usually employed to produce permanent magnets, has increased very quickly. $\text{SrFe}_{12}\text{O}_{19}$ and $\text{BaFe}_{12}\text{O}_{19}$ are cheap but still relatively strong magnets and both have the same crystallographic structure. In this study a mixture of the two was done using difference Sr/Ba ratio. Hydrothermal synthesis was used to produce nanoparticles, which is known to be a fast and clean method allowing accurate control of the reaction parameters. The resulting products were characterized by powder X-ray diffraction, and Rietveld analysis of these data was carried out. The expected trend between the unit cell parameters and the Sr/Ba ratio was observed. Furthermore, an influence on the kinetics of the reaction process was observed. The influence of this substitution on the magnetic properties would be interesting to study in the near future.

Keywords: powder x-ray diffraction, hydrothermal synthesis, permanent magnets

MS09_P110

Internal structure of CdSe quantum dots as derived from total scattering analysis

[Stanislaw Gierlotka^a](#), [Svetlana Stelmakh^a](#), [Kazimierz Skrobas^a](#), [Witold Palosz^b](#) & [Bogdan Palosz^a](#)

^aInstitute of High Pressure Physics, Polish Academy of Sciences, Poland, xray@unipress.waw.pl

^bBrimrose Corporation, USA

Colloidal Quantum Dots (QD) were synthesized using a typical route in non-polar environment [1]. Samples of CdSe nanocrystals (2.5-3 nm in diameter) coated with up to 5 molecular layers of CdS or ZnS were examined. Structural analysis was based on diffraction patterns collected up to Q_{max} of 22 \AA^{-1} using Bruker D8 Advance diffractometer equipped with Ag sealed tube. From the data the $G(r)$ function was derived and analyzed. A new methodology of elaboration of experimental interatomic Pair Distribution Function (PDF) was applied which is based on the assumption that in actual nanocrystals there exist some modulation of atomic density extending from the surface towards the bulk [2]. Such modulation changes average interatomic distances in a nanocrystal and therefore affects the positions of the peaks in PDF. We examined the experimental PDFs in search for the minor displacement of the peaks from the positions they would have if the crystal structure of QD-s was perfectly periodic. In order to understand the observed displacements $G(r)$ -s for atomistic models of nanocrystals with density fluctuation of spherical symmetry - "density waves" were calculated [2]. Simulations and data analysis was performed using computer program NanoPDF developed specifically for those tasks [3]. In the present work we propose tentative models of real atomic architecture of CdSe QD-s. We show a presence of up to 5 "density waves" within the volume of CdSe QDs. The atoms within each wave are shifted from their perfect lattice sites in radial direction by up to 10% of the bond lengths relative to those in the perfect crystal lattice. Correlations between photoluminescence spectra and specific atomic structure of the QDs were also examined.

[1] S.K. Pradhan et al, *J. Appl. Phys.*, 2007, 102, 044304

[2] B. Palosz, E. Grzanka, S. Gierlotka and S. Stelmakh, *Z. Kristallographie*, 2010, 225, 588

[3] K. Skrobas, S. Gierlotka, S. Stelmakh, and B. Palosz, NanoPDF Software Package; <http://www.unipress.waw.pl/soft/crystallography/nanopdf>

Keywords: nanocrystals, quantum dots, pair distribution function, atomic density waves

MS09_P111

Structural studies of MoS₂-based intercalates with organic cations

Alexander S. Goloveshkin, Alexandre S. Golub & Ivan S. Bushmarinov

A.N. Nesmeyanov Institute of Organoelement Compounds, Russia, e-mail: golov-1@mail.ru

One of the important and mild methods for producing layered nanosystems based on molybdenum disulfide (a semiconducting graphene analog) is single-layer dispersion of crystalline MoS₂: reduction of the starting material to (Li)⁺(MoS₂)⁻ and detachment of its layers from each other in aqueous solvents [1].

This dispersion reacts with organic salts in solution, forming layered MoS₂ intercalated with their cations. Most of these compounds have distinct chemical composition and powder X-ray diffraction (PXRD) patterns. These patterns consist of the basal (00l) reflections and the low-intensity hkl zone. Previous studies reported only the positions of the 00l reflections, and the aim of the current work was to extract the information contained in the hkl zone.

In this report, we described the whole PXRD patterns of MoS₂ intercalation compounds and refined their atomic structure.

First, we succeeded in indexing the hkl zone in *pg* plane group using SVD method [2]. This means that the patterns of different (NR₄)_xMoS₂ (R=alkyl, H) compounds consist of only 00l and hk0 peaks, without any hkl (*l*≠0) lines. This fact, in conjunction with highly asymmetric shape of the hk0 lines, suggested that the layers of (NR₄)_xMoS₂ compounds are turbostratically disordered.

Using the obtained unit-cell parameters, the layered structures were Rietveld refined using a modification of a “supercell approach” [3] developed for the full-pattern modeling of disordered clays.

We determined that the Mo atoms in MoS₂ layers in the intercalation compounds have an octahedral coordination, and the S atoms form “nanorunnels” containing organic cations. The refined geometry of the intralayer (-Mo-Mo-)_n chains was consistent with the EXAFS data. The ordering of the organic layer depended on the nature of the cation, with (NEt₄)_xMoS₂ having a structure with specific stoichiometric composition (x=1/6) defined by the intralayer packing. The PW-DFT-d calculations based on this model confirmed our results.

[1] P. Joensen, R.F. Frindt, S.R. Morrison, *Materials Research Bulletin*. 1986, 21, 457

[2] A. A. Coelho, *J. Appl. Cryst.* 2003, 36, 86

[3] K. Ufer, G. Roth, R. Kleeberg, H. Stanjek, R. Dohrmann, J. Bergmann, *Z. Krist.* 2004, 219, 519

Keywords: powder diffraction, layered systems, molybdenum disulphide, Rietveld refinement

MS09_P112

Asbestos fibers origin in Pilsen agglomeration (West Bohemia, Czech Republic) solved by X-ray powder diffraction

David Havlicek^a, Jiri Plocek^b & Miroslav Klan^c

^aDept. of Inorg. Chem., Faculty of Science, Charles University in Prague, Albertov 6, 128 43 Praha 2, Czech Republic, e-mail:havlicek@natur.cuni.cz,
^bInst. of Inorg. Chem. of the ASCR, v.v.i., Husinec – Rez 1001, 250 68 Rez u Prahy, Czech Republic

^cInst. for Environmental Studies, Faculty of Science, Charles University in Prague, Albertov 6, 128 43 Praha 2, Czech Republic

Our work deals with actinolite occurrence in solid fraction of ambient aerosol in Pilsen basin, and its source apportionment. Our technology consists of collection dust particles on glass fibre (non-diffracting) filters in different places around the city and at different meteorological conditions. The filters were worked up by X-ray powder diffraction using parallel-beam geometry and by electron microscopy. The origin of dust and source apportionment was studied with use of direct mineralogical analysis of potential dust sources (transport – engines, tyres, brakes, local burning places, heat plants ashes, building industry, quarries etc.) by X-ray diffraction. The minerals significant for each source were identified and searched on filters collecting atmospheric dust. Great surprise was high content of actinolite in some samples. We have clarified the origin of this mineral in atmospheric dust and identified its resources.

Keywords: atmospheric dust; mineralogical composition; X-ray powder diffraction; parallel beam technique

Thin film morphologies of block copolymers with nanoparticles

Dieter Jehnichen^a, Doris Pospiech^a, Peter Friedel^a, Guping He^a, Alessandro Sepe^b, Jianqi Zhang^b, Christine M. Papadakis^b & Jan Perlich^c

^aLeibniz-Institut für Polymerforschung Dresden e.V., Germany, e-mail: djeh@ippfdd.de

^bTU München, Physik Department E13, Germany, ^cDESY Photon Science Hamburg, Germany

Diblock copolymers (BCP) show phase separation on mesoscopic length scales and form ordered morphologies in both bulk and thin films resulting in nanostructured polymer surfaces [1]. Morphologies in thin films are strongly influenced by film parameters and film thickness related to bulk domain spacings which can be examined by T-dependent SAXS experiments. Laterally structured polymer surfaces may serve as templates for the controlled assembly of nanoparticles.

We investigated BCP of poly(n-pentyl methacrylate) and poly(methyl methacrylate), P(PMA-b-MMA) having different block lengths and compositions which show bulk morphologies with stacked lamellae or hexagonally close-packed cylinders [2]. The BCP were dip-coated onto silicon wafer. The thin films were investigated by atomic force microscopy (AFM) and grazing-incidence small-angle X-ray scattering (GISAXS). For film thicknesses d_f well below d_{bulk} ("repeat distance" controlled by molar masses), standing cylinder morphologies were observed in appropriate molar ratios, while film thicknesses around and larger d_{bulk} resulted in cylinders arranged parallel to the surface.

Functionalization using OH-terminated PMMA blocks worked well as a template for the formation of silica nanoparticles [3], directing the silica particles mainly into the PMMA phase. In order to alter and/or improve the morphology also in presence of different nanoparticles (silica, gold, silver, magnetite) vapor annealing was applied [4,5,6]. In these nanocomposites, the morphology usually remains the same, but the periodicities of nanostructure are changed depending on the type and amount of incorporated nanoparticles. As a common result, it was found that SiO_x clusters enlarge the lateral distance of the cylinders, whereas metallic nanoparticles often rather reduce this parameter. The effect of "vapor annealing" is weak under the conditions chosen so far. In general, the quality of the morphology was slightly improved and the lateral distances kept constant or were slightly reduced.

- [1] D. Jehnichen, D. Pospiech, R. Keska, S. Ptacek, A. Janke, S.S. Funari, A. Timmann, C.M. Papadakis, *J. Nanostruct. Polym. Nanocomp.*, 2008, 4, 119
 [2] D. Jehnichen, D. Pospiech, P. Friedel, S.S. Funary, *Z. Kristallogr. Proc.*, 2011, 1, 487
 [3] S. Werner, D. Pospiech, D. Jehnichen, K. Eckstein, H. Komber, P. Friedel, A. Janke, F. Näther, U. Reuter, B. Voit, R. Taurino, M. Messori, *J. Polym. Sci., Part A: Polym. Chem.*, 2011, 49, 926
 [4] D. Jehnichen, D. Pospiech, P. Friedel, A. Korwitz, A. Berndt, A. Janke, F. Näther, C.M. Papadakis, A. Sepe, J. Perlich, HASYLAB Annual Report 2010, DESY Hamburg
 [5] D. Jehnichen, D. Pospiech, P. Friedel, G. He, C.M. Papadakis, J. Perlich, GISAXS Workshop 2012, DESY Hamburg
 [6] A. Horechyy, B. Nandan, N.E. Zafeiropoulos, D. Jehnichen, M. Göbel, M. Stamm, D. Pospiech, in submission to *Colloid Polym. Sci.*, 2014

Keywords: X-ray scattering, phase separation, thin films, copolymers, nanoparticles

Synchrotron Diffraction Study of Phase Transition in Nano-sized $La_{0.2}Ca_{0.8}MnO_3$

Dmitry Mogilyanski^a, V. Markovich^a & X. D. Wu^b & K. Suzuki^b

^aBen Gurion University of the Negev, Beer Sheva 84105, Israel

^bDepartment of Materials Engineering, Monash University, Clayton, Victoria 3800, Australia
 e-mail: mogily@exchange.bgu.ac.il

Structural properties of $La_{0.2}Ca_{0.8}MnO_3$ nanoparticles with size 15 and 37 nm, prepared by the glycine–nitrate method, have been studied. High resolution synchrotron X-ray powder diffraction patterns were collected on the powder diffraction beamline in Debye-Scherrer transmission configuration at the Australian Synchrotron. The Mythen microstrip detector was used. The experiments performed in the temperature range 80-300 K have shown that below 200K, a structural transition from room temperature orthorhombic *Pnma* phase to monoclinic *P2₁/m* space group, associated with orbital ordering, occurs in the studied particles. Based on X-ray data the temperature dependences of the lattice constants and orthorhombic strains were estimated. It was shown that the phase transformation for the largest 37 nm particles is very close to that one for bulk material. This effect manifested by the temperature variation of the lattice parameters and orthorhombic strain was found to be highly suppressed in smaller 15 nm particles.

Measurements of magnetization of $La_{0.2}Ca_{0.8}MnO_3$ NPs, at low temperatures imply the coexistence of an AFM phase in the core with a minor FM component at the particle surfaces and of a second FM component inside AFM core. The observed effects may be attributed to

the changes in uncompensated surface spins and surface anisotropy or alternatively to a transition in the core from a multi-domain to mono-domain state [1].

[1] V.Marcovich et al. Journal of nanoscience and nanotechnology, 2012, Vol.12 (11), Pp. 8607-8612

Keywords: nanocrystalline manganites, synchrotron radiation, phase transformation

MS09_P115

Nanocrystalline and stacking-disordered AlPO_4 cristobalite the now deciphered main constituent of a municipal sewage sludge ash from a full-scale incineration facility

Burkhard Peplinski^a, Christian Adam^a, Burkart Adamczyk^a, Ralf Müller^a, Matthias Michaelis^a, Thoralf Krahl^b & Franziska Emmerling^a

^aBAM Federal Institute for Materials Research and Testing, Berlin, Germany

^bHumboldt-Universität zu Berlin, Germany
e-mail: burkhard.peplinski@bam.de

Recently, AlPO_4 tridymite was discovered in municipal sewage sludge ashes (SSA) produced at two European incineration facilities [1,2]. The present paper reports on investigations of municipal sewage sludge ash from a third incineration facility serving a catching area with a population of 2 million. For this, tailor-made selective dissolution sample preparation techniques were combined with XRD and XRF analyses of the residues. Thus, evidence was provided that the main component of this SSA can be described as a nanocrystalline, stacking-disordered, non-equilibrium cristobalite form of AlPO_4 . This interpretation is substantiated by synthesis experiments carried out under carefully controlled laboratory conditions providing direct proof that nanocrystalline and stacking-disordered AlPO_4 cristobalite does crystallize under (T,t)-conditions comparable to the vast heating rate and very short retention time (just seconds at $T \approx 850^\circ\text{C}$) typical for fluidized bed incinerators – despite the fact, that the crystallization of the well-crystallized cristobalite form of *pure and stoichiometric* AlPO_4 (or SiO_2) is sluggish even at much higher temperatures. The structural relaxation of this new non-equilibrium and non-stoichiometric phase was followed by XRD over a wide (T,t) range.

[1] Peplinski B., Adam C., Reuther H., Vogel C., Adamczyk B., Menzel M., Emmerling F., Simon F.-G., Z. Kristallogr. Proc.. 2011, Vol. 1, 443 (Proc. EPDIC12, Darmstadt, Germany, 2010

[2] Peplinski B., Adam C., Adamczyk B., Müller R., Schadrack R., Michaelis M., Emmerling F., Reuther H., Menzel M., Powder Diffraction Journal (PDJ). 2013, Vol. 28, Issue S2 p.425 (Proc. EPDIC13, Grenoble, France,2012)

Keywords: aluminum phosphate, cristobalite form, sewage sludge ash, phosphorus recovery

MS09_P116

Preparation and characterization of magnetic nanocomposites in TiO_2 , Al_2O_3 , ZrO_2 , and CeO_2 matrixes

Jiří Plocek^a, Simona Kubičková^b, Alice Mantlíková^b & Jana Vejpravová^b

^aInstitute of Inorganic Chemistry, v.v.i., Academy of Sciences of the CR, 250 68 Rez, Czech Republic, e-mail: plocek@iic.cas.cz

^bInstitute of Physics, v.v.i., Academy of Sciences of the CR, Na Slovance 2, 18221 Prague, Czech Republic

This presentation describes preparation and characterization of magnetic nanocomposite $\text{CoFe}_2\text{O}_4/\text{Al}_2\text{O}_3$, $\text{CoFe}_2\text{O}_4/\text{TiO}_2$, $\text{CoFe}_2\text{O}_4/\text{ZrO}_2$, and $\text{CoFe}_2\text{O}_4/\text{CeO}_2$. First three samples were prepared by newly developed method, which combines hydrothermal and sol-gel methods, which were followed by thermal treatment. $\text{CoFe}_2\text{O}_4/\text{CeO}_2$ was prepared by combination of hydrothermal and controlled precipitation method. All materials were characterized by powder X-ray diffraction, transmission electron microscopy and magnetic measurements.

Cobalt ferrite nanoparticle size was about 5-7 nm in all the samples. $\text{CoFe}_2\text{O}_4/\text{Al}_2\text{O}_3$ samples were stable up to 500°C and their alumina matrix persisted amorphous. $\text{CoFe}_2\text{O}_4/\text{TiO}_2$ samples were stable in all studied temperatures, only amorphous titania recrystallized to anatase and rutile at temperatures beginning from 500°C and 600°C , respectively. $\text{CoFe}_2\text{O}_4/\text{ZrO}_2$ samples were also stable in all studied temperatures. The zirconia matrix recrystallization started at 600°C . All the ceria nanocomposites were thermal treated just at 200°C . The crystallinity of the ceria matrix was controlled not by final thermal treatment, but by modification of preparation conditions. The ceria matrix particle size was about 2 nm.

Keywords: nanocomposite, nanoparticle, sol-gel method, hydrothermal method

Cobalt ferrites nanoparticles obtained by hydrothermal continuous flow synthesis method

Marian Stingaciu^a, Stefano Deledda^b, Matylda Guzik^b, Cesar de Julian Fernandez^{c,d}, Claudio Sangregorio^{d,e} & Mogens Christensen^a

^aDepartment of Chemistry and iNANO, Aarhus University, Denmark, e-mail: stingaciu@chem.au.dk

^bPhysics Department, Institute for Energy Technology, Kjeller, Norway

^cIMEM- CNR, Parma, Italy

^dINSTM - University of Florence, Italy

^eICCOM- CNR Firenze, Italy

Nowadays, there is an increased interest for synthesis of nanoscale magnetic particles due to their importance in the development of technologies such as data storage, permanent magnets or biomedical applications. Among other magnetic materials the cobalt ferrite, CoFe_2O_4 is an interesting material, which in its bulk shape possesses a high saturation magnetization, high coercivity and a good chemical stability¹. The magnetic properties of this material are caused by the superexchange interaction which takes place between the metal cations Co^{2+} and Fe^{3+} and therefore it is strongly influenced by the cations distribution at the tetrahedral and octahedral sites². In turn, the cations distributions is strongly dependent on the particle size, lattice parameters and bond distances between the cations. It is evident that the synthesis route plays an important role in obtaining a material with a controlled cations distribution, as required for the best magnetic properties. In this work nanocrystalline CoFe_2O_4 particles have been produced by supercritical flow synthesis. The structural analysis of produced samples was investigated by means of powder X-ray diffraction and size of the crystallites determined by the Rietveld refinement which turned out to be dependent on the synthesis conditions (7-14 nm). Transmission electron microscopy was used in sample characterization and the particles size distribution estimated. Neutron diffraction study was performed in order to evaluate the cation distribution in the produced nano-size particles which possess the inverse spinel cubic structure at room temperature. Thermomagnetic measurements evidence that the blocking temperature is above room temperature and that nanoparticles exhibit a Curie temperature smaller than the corresponding bulk Curie temperature.

[1] M. Rajendran, R.C. Pullar, A.K. Bhattacharya, D. Das, S.N. Chintalapudi, C.K. Majumdar, *J. Magn. Magn. Mater.* 2001, 232, 71–83.

[2] Z. John Zhang, Zhong L. Wang, Bryan C. Chakoumakos and Jin S. Yin, *J. Am. Chem. Soc.* 1998, 120, 1800–1804.

Keywords: nanoparticles, cobalt ferrite,

Real time investigation of thin film growth in sputter deposition processes

P. Walter^{a,b}, A.-C. Dippel^a, K. Pflaum^a & U. Klemradt^b

^aDeutsches Elektronen-Synchrotron DESY, Hamburg, Germany

^bInstitute of Physics B, RWTH Aachen University, 52056 Aachen, Germany
e-mail: peter.walter@desy.de

Synchrotron radiation of 3rd generation light sources like PETRA III provides the necessary low divergence and high flux of photons to obtain high resolution diffraction patterns as well as additional capabilities of analysis. For instance, the high count rates permit short acquisition times and, thus, time-resolved measurements of structural changes of the sample. These circumstances provide ideal conditions to design implement and operate *in situ* preparation and reaction chambers like a magnetron sputter deposition unit. Radio-frequency sputtering is a common technique to fabricate ultrathin to thick films. We have built a sputtering chamber that is suitable for the use at different synchrotron beam lines for *in situ* measurements [1]. The goal is to investigate lead-free piezoelectric thin films. Structural and compositional control of the piezoelectric layers and the resulting electrical properties requires a fundamental understanding of the whole thin film formation process, from the first interactions at the substrate surface to the structure formation processes during film growth and crystallisation. The focus is set on barium titanate (BaTiO_3), which is used e.g. in thin-film capacitors, non-volatile memories, electro-optical devices and MEMS devices [2,3]. The characteristics of the powders or films strongly depend on the particular choice of processing parameters. Apart from this relation, this work concentrates on the determination of the nucleation, the crystallisation pathway, and the microstructure evolution in BaTiO_3 - layer samples. In order to investigate the film evolution *in situ* using the full capabilities of the synchrotron beam lines the online sputtering chamber designed to be small enough to fit at different diffractometer. Therefore the size and weight of the unit are minimised without limiting the performance of the sputtering process. The presentation reports on results of measurements, the current status of the sputter chamber and in addition the next steps of development.

[1] P. Walter, A.-C. Dippel et al. Annual Report 2012 „Status of the P02.1 RF-Magnetron Sputtering Chamber for in situ Investigation of Thin Film Growth”

[2] George, J. P., et al., *Nanoscale research letters*, (2013) 8(1),62. [3] Y. Drezner, et al., *Appl. Phys. Lett.* 86 (2005) 42906/1.

Keywords: rf magnetron sputtering, synchrotron, powder diffraction, thin films, in situ, time-resolved studies.

*Microsymposium MS10:
Neutron Structural and Magnetic Scattering*

*Chairs: Denis Kozlenko, Joint Institute for Nuclear Research
(Dubna, RU)*

Oksana Zaharko, Paul Scherrer Institut (CH)

Microsymposium: Wednesday 18 June 2014 Morning – iNANO building, 1593-012

Poster session: Monday 16 June 2014 – iNANO building, 1593-012

Keynote Lecturers:

MS10_K1

Correlated Disorder in Functional Materials

[Andrew L. Goodwin](#)

University of Oxford, U.K, e-mail: andrew.goodwin@chem.ox.ac.uk

Crystallography is a technique predisposed towards order. This talk will explore a variety of systems in which *disorder* is actually crucial for function [1]. What role might crystallographic techniques (particularly neutron powder diffraction) play in characterising this disorder? How do we represent and understand structural correlations that have no long-range periodicity and yet are not random? How, as chemists, might we control and exploit this disorder? This talk will try to address these questions, drawing on examples from metal–organic framework chemistry, frustrated magnetism, and the phenomenology of orbital order/disorder transitions in colossal magneto-resistance manganites [2].

[1] A. B. Cairns and A. L. Goodwin, *Chem. Soc. Rev.* **42**, 4881 (2013)
[2] J. A. M. Paddison et al., *Phys. Rev. Lett.* **110**, 267207 (2013)

Keywords: total scattering, neutron diffraction, disorder, functional materials, paramagnetism, orbital order

MS10_K2

Towards sodium ion batteries: understanding sodium dynamics on a microscopic level

[M. Medarde](#)^a, [M. Mena](#)^b, [J.L. Gavilano](#)^b, [E. Pomjakushina](#)^a, [J. Sugiyama](#)^c, [K. Kamazawa](#)^d, [V. Yu Pomjakushin](#)^b, [D. Sheptyakov](#)^b, [B. Batlogg](#)^e, [H.-R. Ott](#)^e, [M. Månsson](#)^{b,e} & [F. Juranyi](#)^b

^aLaboratory for Developments and Methods, Paul Scherrer Institut, CH-5232 Villigen, Switzerland

^bLaboratory for Neutron Scattering, Paul Scherrer Institut, CH-5232 Villigen, Switzerland

^cToyota Central Research & Development Laboratories Inc., Nagakute, Aichi 480-1192, Japan

^dCROSS, Tokai, Ibaragi 319-1106, Japan

^eLaboratory for Solid state physics, ETH Zürich, CH-8093 Zürich, Switzerland

One of the most important scientific problems faced by our society is how to convert and store clean energy. In order to achieve a significant progress in this field we

need to understand the fundamental dynamical processes that govern the transfer of energy on an atomic scale. For many energy devices such as solid-state batteries and solid-oxide fuel cells, this means understanding and controlling the complex mechanisms of ion diffusion in solids.

Because of the unusual evolution of correlated electronic properties (frustrated magnetism and superconductivity), the layered Co-oxide series Na_xCoO_2 ($0 < x < 1$) has been extensively studied during the last decade. More recently it has also attracted the attention of applied sciences, mainly because of its structural similarity with Li_xCoO_2 , one of the most common electrode materials in Li-ion batteries. In view of the larger abundance of Na in the earth crust with respect to Li, we have investigated the Na-ion diffusion in Na_xCoO_2 , whose possible use as cathode material for solid-state rechargeable batteries has recently been proposed [1].

The present study reports the observation of a crossover from quasi-1D to 2D Na-ion diffusion in $\text{Na}_{0.7}\text{CoO}_2$. Using high resolution neutron powder diffraction we observed two structural transitions at $T_1=290\text{K}$ and $T_2=400\text{K}$ [2]. Analyses of the anomalies in the Na-Na distances, the Debye-Waller factors and the scattering density in the paths connecting neighboring Na sites strongly suggest that both transitions are related to changes in the Na-ion mobility. Our data are consistent with a two-step diffusion mechanism through the successive opening of first quasi-1D ($T_1 < T < T_2$) and then 2D ($T > T_2$) Na diffusion paths [2]. These findings provide new insight on the subtle mechanisms controlling the Na-ion diffusion in the Na_xCoO_2 series and could be used for the design of related materials with improved functional properties in energy applications.

[1] A. Bhide et al., *Solid State Ionics* **192**, 360 (2011)
[2] M. Medarde et al. *PRL* **110**, 266401 (2013)

Keywords: Na-ion batteries, Neutron powder diffraction, Na diffusion

MS10_O1

Interplay between spin and lattice degrees of freedom in VF₃

G. Nénert^a, P.G. Reuvekamp^b, C. Drathen^c, R. Eger^b, F. Kraus^d & J. Köhler^b, R. K. Kremer^b

^aPAAnalytical, Lelyweg 7602 EA, Almelo, The Netherlands

^bMPI fuer Festkoerperforschung Heisenbergstrasse 1v D-70569 Stuttgart Germany

^cESRF, BP220, 38043 Grenoble Cedex, France

^dTechnische Universität München, Lichtenbergstrasse 4, 85747 Garching, Germany

We report on a magnetic and structural investigation of layered antiferromagnetic system vanadium (III) fluoride. VF₃ crystallizes in a distorted ReO₃ structure (R-3c) with rotated undistorted VF₆ octahedra. The V³⁺ cations are arranged in a triangular lattice with the possibility of exhibiting magnetic frustration. Polycrystalline samples of VF₃ were investigated using heat capacity, dielectric, magnetic susceptibility, synchrotron and neutron powder diffraction methods. Combining our results, we report the first evidence for a first order phase transition resulting from the ordering of the t_{2g} orbitals below 105-110 K. This transition reduces the symmetry to C2/c. We further confirm that VF₃ undergoes a long-range antiferromagnetic order at ~19 K in accordance with literature [1]. The antiferromagnetic order results in a magnetic structure with the magnetic moments alternating between a parallel and b parallel alignments in the ab plane

[1] A.C. Gossard, H.J. Guggenheim, F.S.L. Hsu, and R.C. Sherwood, AIP Conf. Proc., No. 5, 302 (1971).

Keywords: orbital ordering, fluoride, magnetism, powder diffraction

Nature of Partial Magnetic Order in Gd₂Ti₂O₇

Joseph Paddison^{a,b}, Andrew Goodwin^a, Dmitry Khalyavin^b, Pascal Manuel^b, Georg Ehlers^c, Oleg Petrenko^d, Jason Gardner^e & Ross Stewart^b

^aUniversity of Oxford, U.K., email:joseph.paddison@chem.ox.ac.uk

^bSTFC-ISIS, Rutherford Appleton Laboratory, U.K.

^cSNS, Oak Ridge National Laboratory, USA

^dUniversity of Warwick, U.K.;

^eANSTO, Australia

Most magnetic materials form conventional periodic magnetic order at low temperature. An exception to this rule is the frustrated pyrochlore system Gd₂Ti₂O₇, which forms a partially-ordered phase below $T_N \sim 1$ K, defying theoretical expectations [1]. In this phase, the magnetic propagation vector $\mathbf{k} = (1/2, 1/2, 1/2)$ results in a 1:3 splitting of the crystallographically-equivalent Gd site such that three-quarters of the spins have an ordered moment close to the maximum allowed ($7 \mu_B$) while the remaining quarter retain a large paramagnetic component [2]. Magnetic structure determination is further complicated because the Bragg component of powder diffraction cannot determine whether the structure consists of a single propagation vector ($1\mathbf{k}$ structure) or is a superposition of several propagation vectors (multi- \mathbf{k} structures). Based on an analysis of the diffuse scattering from the paramagnetic spins, it has previously been proposed that the structure is $4\mathbf{k}$ [3]. However, using in-field single-crystal diffraction, we find that the $4\mathbf{k}$ -structure is definitively ruled out for Gd₂Ti₂O₇. This has led us to return to powder diffraction data in order to understand how the observed diffuse scattering can actually be compatible with a $1\mathbf{k}$ (or other alternative) structure. We have used newly-developed reverse Monte Carlo software [4] to analyse both the diffuse and Bragg contributions to the powder diffraction data simultaneously, and to develop a model of magnetic disorder in Gd₂Ti₂O₇.

[1] Palmer, S. E. & Chalker, J. T. *Phys. Rev. B.* 2000, 62, 488

[2] Champion, J. D. M., Wills, A. S., Fennell, T. & Bramwell, S. T. *Phys. Rev. B.* 2001, 64, 140407

[3] Stewart, J. R., Ehlers, G., Wills, A. S., Bramwell, S. T. & Gardner, J. S. *J. Phys.: Condens. Matter.* 2004 16, L321

[4] Paddison, J. A. M & Goodwin A. L. *Phys. Rev. Lett.* 2012, 017204

Keywords: magnetism, diffuse scattering, frustration

MS10_O3

Powder Diffraction Study of Structural and Magnetic Transitions in Oxygen Deficient Complex Cobalt Oxides

Vadim Sikolenko^a, Igor Troyanchuk^b, Vadim Efimov^c, Ekaterina Efimova^c, Antonio Cervellino^d, Clemens Ritter^e, Dmitry Karpinsky^b, Thomas Hansen^e, Maxim Bushinsky^b & Susan Schorr^a

^aHelmholtz Center Berlin, Germany, e-mail: vadim.sikolenko@hmi.de

^bMaterial Research Center of NAN, Belarus

^cJoint Institute for Nuclear Research, Russia

^dPaul Scherrer Institute, Switzerland

^eInstitute Laue Langevin, France

Oxygen content in La(Ba,Sr)CoO_x can be varied in a wide range, that leads to a change of average oxidation state of the cobalt ions. We have studied structural and magnetic properties of La_{0.5}(Ba, Sr)_{0.5}CoO_{3-x} solid solutions with a oxidative state of cobalt close to 3+ by X-ray and neutron diffraction in a wide temperature region [1,2] at ambient and external pressure till 6 GPa [3,4]. Possible mechanisms of phase separation and magnetic interaction between Co ions in different spin states are discussed.

-
- [1] I.Troyanchuk et.al. , *JETP Lett* 2014, 93, 149
[2] D.Karpinsky et.al., *J.Phys.:Cond.Mat.* 2013, 25, 316004
[3] I.Troyanchuk et.al. , *Eur.Phys.J.B* 2013, 86, 435
[4] V.Sikolenko et.al. , *Powder Diffr.* 2013, 28, S126

Keywords: neutron powder diffraction, phase separation, cobaltites, magnetic structure

MS10_O4

Electric polarization from spiral order below 200K in multiferroic YBaCuFeO₅

Mickaël Morin^a, Denis Scheptyakov^b, Lukas Keller^b, Juan Rodríguez-Carvajal^c, Andrea Scaramucci^d, Nicola Spaldin^d, Michel Kenzelmann^a, Ekaterina Pomjakushina^a, Kazimierz Conder^a & Marisa Medarde^a

^aLaboratory for Developments and Methods, Paul Scherrer Institut, 5232 Villigen PSI, Switzerland

^bMaterials Theory, ETH Zurich, Wolfgang-Pauli-Strasse 27, CH-8093 Zurich, Switzerland

^cInstitut Laue-Langevin, BP 156X, F-38042 Grenoble, France

^dLaboratory for Neutron Scattering, Paul Scherrer Institut, 5232 Villigen PSI, Switzerland

Ferroelectric materials have been known for almost one century [1]. While their potential for applications was rapidly recognized, the possibility of combining ferroelectricity with magnetic order -preferably with

ferromagnetism- has resulted in an enormous deal of interest during the last decade. Several new materials combining both types of order have been recently reported, although their promising multifunctionalities have been obscured by two facts: on one side, most of them are antiferromagnetic; on the other, their transition temperatures, typically below 40K, are too low for most practical applications.

The oxygen-deficient double perovskite YBaFeCuO₅ constitutes a remarkable exception. Spontaneous electric polarization has been recently reported to exist below an unusually high temperature of T_C ≈ 200K [2] coinciding with the occurrence of a commensurate - to - incommensurate reorientation of the Fe³⁺ and Cu²⁺ magnetic moments [3,4]. From a more fundamental point of view the observation of incommensurable magnetic order in a tetragonal material at such high temperatures is rather surprising. In particular, the nature of the relevant competing magnetic interactions and its possible link to low dimensionality or geometrical frustration is not understood at present.

Although the existence of the spin reorientation in this material is known since 1995 [3] the low temperature magnetic structure has not yet been solved. Using neutron powder diffraction we have recently been able to propose a spiral model which satisfactorily describes the measured magnetic intensities below T_C [4]. Further, investigation of the crystal structure showed the existence of small anomalies in the lattice parameters and some interatomic distances at T_C. The relevance of these findings for the magnetoelectric coupling, the direction of the polarization, the modification of the different exchange paths in the structure and the stabilization of the incommensurate magnetic order below T_C will be discussed.

-
- [1] J. Valasek *Physical Review* **15**, 537(1920)
[2] B. Kundys et al., *Appl. Phys. Lett.* **94**, 072506, (2009).
[3] V. Caignaert et al., *J. Solid State Chem.* **114**, 24, (1995).
[4] M. Morin et al., in preparation

Keywords: Multiferroic, Neutron powder diffraction, Spiral magnetic order

Posters:

MS10_P119

Representation Analysis in Neutron Diffraction Studies of the Anomalous Behavior of Magnetic Structure in Terbium Iron Garnet

Mahieddine Lahoubi^a

^aUniversity of Badji Mokhtar Annaba, 23000 Annaba, Algeria, e-mail: mlahoubi@hotmail.fr

The representation analysis of Bertaut [1, 2] has been used in the interpretation of the neutron powder diffraction data obtained recently on terbium iron garnet [3-5]. Lowering the temperature (T) below the Néel point ($T_N \approx 568$ K) [6], two successive increases, near 160 K and between 54 and 68 K are present in the thermal variations of the observed and calculated reflections (hkl) indexed with the general extinction rule $h + k + l = 2n$ of the cubic space group $Ia\bar{3}d$ with $k = 0$ such those which have a great magnetic contribution $\{(211), (321), (521) \text{ and } (532, 611)\}^2$.

At the contrary, the set of reflections such those where the nuclear and magnetic contributions of the iron ions in the octahedral site [16a] are present, $\{(220), (620) \text{ and } (440)\}$, shows anomalous T evolutions with an increase from 4.2 to 160 K and an inflexion point near 54-68 K range. Above 160 K, they tend to a plateau around 300 K after which, they decrease progressively up to T_N .

Based on the best refined magnetic moment vectors m_1 and m'_1 associated respectively to the two sublattices C_1 and C'_1 of the “double umbrella” [3-5], we use the pertinent parameters $\Delta m = |m_1 - m'_1|$ and $\Delta\theta = |\theta_1 - \theta'_1|$, where (m_1, θ_1, ϕ_1) and $(m'_1, \theta'_1, \phi'_1)$ are the corresponding spherical coordinates. They reach their greatest values near 54 K. After a decreasing with increasing T , Δm and $\Delta\theta$ disappear above 160 K in agreement with the T dependences of the pure magnetic superstructure lines (hkl)^{*} such $\{(110)^*, (310)^*, (411, 330)^* \text{ and } (530, 433)^*\}$. The results are discussed in relation with the theory of the low-temperature point of Belov T_B predicted at 58 K [6] and to the recent magnetodielectric effects found in this compound [7].

[1] E. F. Bertaut, *Acta Cryst.* 1968, A24, 217

[2] E. F. Bertaut, *J. Magn. Magn. Mater.* 1981, 24, 267

[3] M. Lahoubi, “Temperature evolution of the double umbrella magnetic structure in terbium iron garnet”, in *Neutron Diffraction*, (Ed) I. Khidirov, 2012, Chap. 10, pp. 203-230

[4] M. Lahoubi, *Journal of Phys. Conf. Ser.* 2012, 340, 012068

[5] M. Lahoubi and B. Ouladdiaf, in press DOI:

<http://dx.doi.org/10.1016/j.jmmm.2014.02.015>

[6] K. P. Belov, *Phys. Ups.* 1996, 39, 623

[7] N. Hur *et al.*, *Appl. Phys. Lett.* 2005, 87, 042901.

Keywords: rare earth iron garnet, ferrimagnetism, neutron diffraction intensity, double umbrella, magnetic moment, ‘low-temperature point of Belov’ T_B

*Microsymposium MS11:
Structure and properties of functional materials*

Chairs: Matt Tucker, ISIS Facility (UK)

Helmut Ehrenberg, KIT, IAM-ES (Karlsruhe, DE)

Microsymposium: Tuesday 17 June 2014 Afternoon – iNANO building, 1593-012

Poster session: Tuesday 17 June 2014 – Chemistry AUD VI, 1510-213

MS11_K1

Neutron Diffraction Studies of Fuel Cell Materials

Stephen Hull^a

^aThe ISIS Facility, STFC Rutherford Appleton Laboratory, Chilton, Didcot, Oxfordshire, OX11 0QX, UK.

Powder diffraction techniques are used extensively to probe the structure-property relationships within materials of technological relevance in the fields of energy production and storage. In particular, neutron powder diffraction studies have advantages in terms of locating light atoms in the presence of heavier ones, since many of the promising compounds for use as electrodes and electrolytes in battery and fuel cell technologies rely on rapid diffusion of ions such as H⁺, Li⁺ and O²⁻ through the solid. Clearly, a complete characterization of the structures of these inherently disordered systems, and the relationship to the ionic motion, is essential to understanding the behavior of existing compounds and identifying promising routes to new materials with improved performance.

This presentation will summarise recent neutron powder diffraction studies of selected ‘energy materials’ performed at the ISIS spallation neutron source, with particular emphasis on oxide-ion conducting ceramics for use in Solid Oxide Fuel Cell (SOFC) technologies. Specific topics to be covered include the following :

(i) The use of ‘total scattering’ methods (*i.e.* utilising both the Bragg and diffuse scattering components), including reverse Monte Carlo analysis of the data to probe the nature of the defects within the materials [1,2]. (ii) The complimentary use of neutron powder diffraction and Molecular Dynamics simulations to investigate the nature of the ionic diffusion mechanisms and the factors which promote extensive oxide-ion diffusion [3,4]. (iii) The development of novel sample environment devices to allow neutron powder diffraction studies of SOFC electrolyte materials to be performed under conditions of temperature and gas atmosphere which mimic those found in real device applications [5].

-
- [1] S. Hull et al, *Dalton Trans.* 2009, 8737-8745
[2] S. Hull et al, *J. Solid State Chem.* 2009, 2815-2821
[3] S.T. Norberg, et al, *Chem. Mater.* 2011, 23, 1356-1364
[4] D. Marrocchelli et al, *Chem. Mater.* 2011, 23, 1365-1373
[5] R. Haynes et al, *J. Phys. Conf. Ser.* 2010, 251 012090

Keywords: neutron diffraction, in-situ studies, oxide-ion conductors, Solid Oxide Fuel Cells.

Local Off-Centering Symmetry Breaking in the High-Temperature Regime of SnTe

Emil Bozin^a, Kevin Knox^a, Christos Malliakas^{b,c}, Mercouri Kanatzidis^{b,c} & Simon J.L. Billinge^{a,d}

^aBrookhaven National Laboratory, Upton, NY, USA, bozin@bnl.gov,

^bNorthwestern University, Evanston, IL, USA

^cArgonne National Laboratory, Argonne, IL, USA

^dColumbia University, New York, NY, USA

The local structure of SnTe has been studied using atomic pair distribution function analysis of x-ray and neutron total scattering data. Evidence is found for a locally distorted high-temperature state, which emerges on warming from an undistorted rock-salt structure. The structural distortion appears rapidly over a relatively narrow temperature range from 300 K to 400 K. A similar effect has been reported in PbTe and PbS [1] and dubbed emphanisism [2]; here we report on emphanisism in a compound that does not contain Pb. The analysis suggests that this effect is unrelated to the low-temperature ferroelectric state in SnTe [3]. The nature of the emphanitic behavior in SnTe allows us to answer key questions about the effect. First, it is not, as previously supposed, related to fluctuations of the incipient ferroelectric state of the material. Second, as indicated by the abrupt temperature response, it is unlikely to originate from simple anharmonic effects. Pb and Sn both possess an electron lone pair (LP) which can be in an active (LPA: resulting in a low-symmetry structure) or inactive (LPI: resulting in a high-symmetry structure) state depending on the compound in question. A possible explanation for emphanisism is a crossover from an LPI state at low temperature to an LPA state at high temperature, brought on by the dramatic lattice expansion in these materials. Our results suggest that there may be a broad class of compounds that display emphanitic behavior, prompting further studies to identify these materials. Additionally, theoretical calculations and modeling of the physical properties of the IV–VI materials already identified should take the emphanitic behavior into account.

-
- [1] E.S. Bozin *et al.*, *Science* 2010, 330, 1660
[2] K. M. Ø. Jensen *et al.*, *Phys. Rev. B* 2012, 86, 085313
[3] K. R. Knox *et al.*, *Phys. Rev. B* 2014, 89, 014102.

Keywords: Ferroelectrics, Nanometer Scale Heterogeneities, Thermoelectrics

MS11_O1

Structure, electric and magnetic properties of $\text{Pb}(\text{V}_{1-x}\text{M}_x)\text{O}_3$, $\text{M}=\text{Ti, Fe}$ compounds

Pierre Bordet^{a,b}, Alexandru Okos^{a,b,c}, Claire Colin^{a,b}, Céline Darie^{a,b} & Aurel Pop^c

^a Univ. Grenoble Alpes, Institut Néel, Grenoble, France,
^b CNRS, Institut Néel, Grenoble, France

^c Babes-Bolyai University, Faculty of Physics Cluj-Napoca, Romania)

Ferroelectricity and magnetic order are considered as hardly compatible in perovskite compounds. In this respect, PbVO_3 is quite interesting: it is isostructural to ferroelectric PbTiO_3 (space group $P4mm$) and contains V^{4+} spin $\frac{1}{2}$ cations [1]. However, previous studies have failed to observe magnetic order in PbVO_3 . This was attributed to a 2D magnetic behaviour or to magnetic frustration on a square lattice [2]. We present the study of V^{4+} substitution by Fe^{3+} or Ti^{4+} cations, aiming at better understanding the relations between structural, magnetic and electric properties.

PbVO_3 single crystals and powders of substituted compounds were prepared at 6GPa, 950°C in belt and Conac devices. A single crystal diffraction experiment confirmed the proposed structure for PbVO_3 , evidencing merohedral twinning related to ferroelectric domains observed by SEM. For Ti substitution, a complete solid solution is observed, while the Fe substitution stops at $x=0.5$ due to heterovalent cation replacement, the formula being $\text{Pb}(\text{V}_{1-2x}^{4+}\text{V}_x^{5+}\text{Fe}_x^{3+})\text{O}_3$. The cation oxidation states were checked by XANES (FAME-ESRF). The structures were studied by joint refinements of NPD (D1B-ILL) and XPD (Laboratory and ID31-ESRF) data, yielding the coordinations of V and M cations and the spontaneous polarization using a point charge model. A decrease of tetragonality, correlation length along the c-axis and polarization is observed with increasing substitution.

For the Ti series, the magnetic behaviour progressively changes from 2D to Curie-Weiss with increasing x . In the case of Fe, a broad peak in magnetic susceptibility is observed, at temperatures increasing from 12K to 30K for x going from 0.1 to 0.5. This was checked as due to a spin glass like behaviour. No sign of magnetic order was observed by NPD. At the same time, a broad, frequency dependent anomaly of the dielectric constant was observed, reminiscent of a relaxor behaviour.

[1] R. V. Shpanchenko, V. V. Chernaya, A. A. Tsirlin et al. Chem. Mater., 16 (17), 3267, 2004

[2] A. A. Tsirlin, A. A. Belik, R. V. Shpanchenko et al. Phys. Rev. B 77, 092402, 2008

Keywords: High pressure, Perovskite, multiferroics

Study of Charge-ordering in $\text{Pr}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ via Serial Femtosecond Crystallography

Kenneth R. Beyerlein^a, Lorenzo Galli^a, Henry Chapman^a, Michael Foerst^b, Roman Mankowsky^b, Andrea Cavalleri^b & Christian Jooss^c

^aCenter for Free-Electron Laser Science, Germany, ^bMax Plank Institute for the Structure and Dynamics of Matter, Germany, ^cUniversity of Goettingen, Germany

e-mail: kenneth.beyerlein@cfel.de

Some rare-earth manganites exhibit a metal-insulator transition which is attributed to long range charge-ordering in the lattice. In order to accommodate this electronic structure the lattice of the manganite becomes slightly distorted. However, the coupling and causation between the electronic and structural reordering is currently a topic of research.

In this light, initial experiments were performed at the Coherent X-ray Imaging (CXI) beamline of the LINAC Coherent Light Source (LCLS) to investigate the charge-ordered structure of $\text{Pr}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$. The data analysis and sample delivery methods of serial femtosecond crystallography, which have been developed to facilitate protein structure determination, were extended to study this novel condensed matter system. Measurements were made on sub-micron manganite particles flown in a micron-sized stream of ethanol which was cooled to 200 K in a cooling nozzle. More than 70,000 diffraction patterns from different isolated nanoparticles were collected. Evidence of clearly distinguishable charge-ordered super lattice peaks in the data will be presented. Also, it will be discussed how analysis of the Bragg spot shapes in the many diffraction patterns provides unique information about the microstructure surrounding this transformation.

Keywords: manganites, charge-ordering, serial femtosecond crystallography, x-ray free-electron laser

MS11_O3

Location of CO₂ guest molecules during its uptake by the flexible porous MOF MIL-53(Fe)

Nathalie Guillou^a, Richard I. Walton^b, Philip L. Llewellyn^c & Frank Millange^a

^aILV, University of Versailles, France

^bDepartment of Chemistry University of Warwick, UK

^cMADIREL, Aix-Marseille University, France

e-mail: nathalie.guillou@uvsq.fr

Metal Organic Framework (MOF) materials are constructed from metal centres linked by polydentate ligands to yield open framework structures. They have found huge interest since the last few years in applications as diverse as separation, storage or drug delivery. Some of them are able to adapt their pore opening to accommodate guest species with drastic changes in cell volume and without a loss of crystallinity or bond breaking. This effect called “breathing” can be illustrated by the group of materials MIL-53(M) (M = Cr Al Ga and Fe) (MIL = Materials from Institut Lavoisier) or M^{III}(OH)₂[O₂C-C₆H₄-CO₂] which can be described as a one-dimensional channel system made up of *trans*-linked Me^{III} octahedra crosslinked by the bidentate dicarboxylate. This material is able to take up various guest molecules [1], nevertheless their precise localization is still limited [2]. This study deals with the uptake of CO₂ by MIL-53(Fe). Adsorption isotherms show that this uptake occurs in three steps. Synchrotron data of the corresponding compounds were collected at ESRF on the ID31 beamline equipped with a gas cell which allows samples contained in thin-walled glass capillaries to be dosed with gas up to 60 bars. The transition between the activated sample [3] to the MIL-53(Fe)_{np}0.63CO₂ [S.G. *C2/c* ; *V* = 1083.01(2) Å³] which presents statistic occupancy of all tunnels by CO₂ occurs through the presence of the intermediate MIL-53(Fe)_{int}0.22CO₂ [S.G. *P-1* ; *V* = 916.80(6) Å³] in which only one out of two tunnels is filled by CO₂ molecules. Under higher CO₂ pressure the MIL-53(Fe)_{lp}2.72CO₂ [S.G. *Imcm* ; *V* = 1563.10(4) Å³] is obtained. A precise localization of CO₂ molecules has lead us to conclude that this uptake is mainly governed by hydrogen bonds between framework μ₂-OH and oxygen atoms of CO₂ molecules. These results will be compared to those previously obtained on similar materials based on molecular simulation [4].

[1] El Osta R., Carlin-Sinclair A., Guillou N., Walton R. I., Vermoortele F., Maes M., de Vos D., Millange F., *Chem. Mat.* 2012, 24 (14) 2781-2791.

[2] Devic T., Salles F., Bourrelly S., Moulin B., Maurin G., Horcajada P., Serre C., Vimont A., Lavalley J.C., Leclerc H., Clet G., Daturi M., Llewellyn P.L., Filinchuk Y., Férey G., *J. Mater. Chem.*, 2012, 22, 10266–10273.

[3] Millange F., Guillou N., Walton R. I., Grenèche J. M., Margiolaki I., Férey, G., *Chem. Commun.*, 2008, (39), 4732-4734.

[4] Chen L., Mowat J.P.S., Fairen-Jimenez D., Morrison C.A., Thompson S.P., Wright P.A., Düren T., *J. Am. Chem. Soc.*, 2013, 135, 15763-15773.

Keywords: MOFs, Porous, Adsorption, CO₂

MS11_O4

Mapping topology and structural disorder in [M(CN)₂]⁻ coordination polymers

Joshua A Hill^a, Andrew B Cairns^a & Andrew L. Goodwin^a

^aDepartment of Chemistry, Inorganic Chemistry Laboratory, University of Oxford South Parks Road, Oxford, OX1 3QR, UK
e-mail: joshua.hill@chem.ox.ac.uk

Dicyanometallate coordination polymers show a number of desirable properties: piezoelectricity, record-breaking negative thermal expansion (NTE) and negative linear compressibility (NLC), vapochromism, and luminescence[1-3]. Despite this, the rules governing the structural trends arising from the use of this ~10 Å linker, [M(CN)₂]⁻ where M = Cu, Ag, or Au, are relatively poorly explored. This talk is concerned both with mapping the composition–connectivity relationship in these systems and understanding the role of guest cation size/shape mismatch. We show that using guest cations that would be a poor fit for the void-space in commonly adopted topologies can lead to two structural phenomena exemplified in compounds reported here. Firstly, the adoption of unusual topologies, such as 5-connected frameworks e.g. [Bu₄N]_{0.5}Cd[Ag(CN)₂]_{2.5} and secondly, correlated structural disorder as seen in molecular perovskite analogues [Bu₄N]M[Au(CN)₂]₃ where M = Cd, Mn, Fe.

[1] S. C. Abrahams *et al.*, *J. Chem. Phys.*, 1980, 73(9), 4585

[2] J. Lefebvre *et al.*, *Sensors*, 2012, 12(3), 3669

[3] A. B. Cairns *et al.*, *Nature Mater.*, 2013, 12(3), 212

Keywords: coordination polymers, perovskite analogues, cyanide

MS11_P120

Characterization of White clinker Cement: Discussion related defects

Ben Haj Amara Abdessalem, Benmohamed Mohamed & Alouani Rabah

Laboratory of Physics of Lamellar hybrid Materials and Nanomaterials,
Faculty of Science of Bizerte, Zarzouna 7021, TUNISIA,
Abdessalem.bha@gmail.com; medbenmohamed85@gmail.com;
rabeh_alouani@yahoo.fr

The clinkerisation is the most important step in the production of white Portland cement (participating at 90% the cost of cement production). Indeed, in some cases the product clinker company is in disagreement with norms. For economic and environmental reasons, the clinker should be recycled back into raw. So any defect in the clinker will be recorded to the energy cost. We find it useful to analyze these clinkers to identify different phases and associated defects. Several analysis techniques can be used to characterize white clinkers. This study was achieved using chemical measuring out, XRF, XRD and SEM analyses.

The results obtained showed that the defects detected in these clinkers are the following:

Fluctuation of the amount of principal phases (alite (C3S) and belite (C2S)),

Excess of liquid phase and free lime,

Presence of C3S polymorph (triclinic, monoclinic and rhombohedral) indicating a low temperature furnace,

Presence of moderately crystallized structures.

Keywords: Portland Clinker, White Cement, Mineralogy, XRF, XRD, SEM, Polymorph, Defects Related to Clinker

Non-triglyceride structuring of edible oils and emulsions

Ruud den Adel^a, Arjen Bot^a, Eli Roijers^a, Patricia Heussen^a & Eckhard Flöter^b

^aUnilever Research & Development Vlaardingen, The Netherlands,
^bTechnical University, Berlin, Germany,
e-mail:ruud-den.adel@unilever.com

The structure of oil-continuous products, such as margarine or butter, is based on a network of small crystallites of triglycerides (also known as triacylglycerols or TAGs). Low molecular weight structuring agents that can serve as an alternative to crystallising triglycerides in edible oils have raised considerable interest in recent years. The requirement that potential structurants should at least hold the promise to be allowed in food applications is a severe limitation. Nevertheless, several systems have been identified [1], amongst which the class of γ -oryzanol + sterol organogelators is the most intriguing representative [2].

Small-angle X-ray scattering (SAXS) studies demonstrated that mixtures of β -sitosterol and γ -oryzanol form tubules in triglyceride oil with a diameter of 7.2 ± 0.1 nm and a wall thickness of 0.8 ± 0.2 nm [3]. Mixtures of β -sitosterol and γ -oryzanol in emulsions at 16% total sterols show scattering data containing reflections of mainly β -sitosterol mono-hydrate crystals. Evidence for the formation of tubules is not found in these emulsion systems, indicating that transitions from anhydrous and hemi-hydrate to monohydrate formation prevent this self-assembled supra-molecular ordering. Intermolecular hydrogen bonding is playing an important role in the formation of the tubules and hydration of sterols might exclude the appearance of this bonding [4].

The stability of the tubules in the presence of water is critical for the applicability of these organogelling systems in the structuring of food emulsions. A decrease of the water activity by salt suppresses the hydration of sterols and promotes tubule formation.

[1] Perneti M, van Malssen KF, Flöter E., Bot A: Structuring of edible oils by alternatives to crystalline fat, *Current Opinion in Colloid and Interface Science* 12 (2007) 221-231. [2] Bot A, Agterof WGM: Structuring of edible oils by mixtures of γ -oryzanol with β -sitosterol or related phytosterols, *Journal of the American Oil Chemists' Society* 83 (2006) 513-521. [3] Bot A, den Adel R, Roijers EC: Fibrils of γ -oryzanol + β -sitosterol in edible oil organogels, *Journal of the American Oil Chemists' Society* 85 (2008) 1127-1134. [4] R. den Adel, P.C.M. Heussen and A. Bot, Effect of water on self-assembled tubules in β -sitosterol + γ -oryzanol-based organogels, *Journal of Physics: Conference series* 247 (2010) 012025.

Keywords: Organogels, Edible oils, SAXS, β -sitosterol, γ -oryzanol, tubules

MS11_P122

Study on interaction between M^{II}: Al Layered Double Hydroxides (M^{II} = Mg²⁺ and Zn²⁺) and Berberine Chloride (BC)

Ben Haj Amara Abdesslem, [Djebbi Med Amine](#), Charradi Khaled & Ben Rhaïem Hafsia

Laboratory of Physics of Lamellar Materials and Hybrid Nano-Materials (PLMHNM), Faculty of Sciences of Bizerte, 7021 Zarzouna, Tunisia
abdesslem.bha@gmail.com; med-djebbi@hotmail.fr;
charradi_kaled2000@yahoo.fr; benrhaïem_hafsia@yahoo.fr

Layered double hydroxides (LDHs) can be structurally described by the stacking of positively charged layers with host anionic species in the interlayer space. These materials can be used as an excellent matrix for biomolecule immobilization. This work aims at studying the interaction between M^{II}: Al Layered Double Hydroxides (LDHs) (M^{II} = Mg²⁺ and Zn²⁺) and Berberine Chloride (BC) with two mechanisms: simple adsorption and direct co-precipitation.

The adsorption experiments of Berberine Chloride on LDHs were evaluated under laboratory conditions with particular attention given to layer charge effect, matrix host and morphology of matrix. The immobilization by adsorption highlighted low capacities of adsorption.

Whereas the co-precipitation mode, achieved using different BC/LDH ratios, allows increasing the amount of immobilized biomolecules. The structural study was carried out by means of X-Ray Diffraction (XRD) and Infrared Spectroscopy (IR). Examination of XRD lines shows that there is no shift of Bragg's angles to low values. This indicates that the immobilization process does not lead to Berberine Chloride intercalation into the LDH layers. The preservation of the spatial configuration and biological activities of the Berberine Chloride showed that LDHs can be like host matrices for the immobilization of Berberine.

Keywords: Layered Double Hydroxides (LDH), Berberine Chloride (BC), Adsorption, Co-precipitation

MS11_P123

Structure Investigation of Ferrite Ceramics Synthesized by Radiation-Thermal Technique

[Uliana V. Ancharova](#)^a, [Mikhail A. Mikhailenko](#)^a, [Boris B. Tolochko](#)^a & [Mikhail V. Korobeynikov](#)^b

^aInstitute of Solid State Chemistry and Mechanochemistry SB RAS, Russia,
^bBudker Institute of Nuclear Physics SB RAS, Russia
e-mail: ancharova@gmail.com

Investigations of the influence of irradiation with intense beams of relativistic electrons on the kinetics of the high-temperature synthesis have shown [1-4] that under electron irradiation the synthesis is significantly accelerated at relatively low temperatures for a number of different oxide systems (NaFeO₂, BaTiO₃, NiFe₂O₄, LiFe₅O₈, MnFe₂O₄, ZnFe₂O₄ and many others). It is shown that the electron beam is a powerful factor in the amplification of solid phase reactions, at least when the reaction rate is determined by the diffusion of the reagents.

This work aims to study the products of radiation-thermal reaction in the synthesis of ferrite ceramic materials under irradiation with an intense beam of electrons with energy of 2.4 MeV. The reaction mixtures have been prepared by joint mechanical activation of the reactants in a ball-mill.

By synchrotron radiation X-ray diffraction methods the kinetics of different chemical reactions are compared: radiation-thermal reactions in *ex situ* mode, and *in situ* reactions of thermal synthesis of the same ceramic materials without irradiation. *In situ* investigations are carried out with continuous X-ray diffraction frame-by-frame exposing by 1D or 2D-detector at synchrotron radiation. The resulting powders of ceramic materials are studied for the phase composition, chemical homogeneity, defects in the structure. The analysis of various irradiation conditions on the phase composition, nano- and microstructure of obtained oxides are performed. A comparison of the reactivity of mechanically activated mixtures derived from commodity oxides and from nano-oxides of metals is made. It is shown that for the effective reaction the formation of the mechanocomposite is necessary.

This work was carried out with the involvement of equipment belonging to the shared research center "SSTRC" (supported by the Ministry of Education and Science of the Russian Federation).

[1] N. Z. Lyakhov, V. V. Boldyrev, A. P. Voronin, O. S. Gribkov, L. G. Bochkarev, S. V. Rusakov & V. L. Auslender, *Journal of Thermal Analysis*. 1995, 43, 21 [2] V.V. Boldyrev, A.P. Voronin, O.S. Gribkov, E.V. Tkachenko, G.R. Karagedov, B.I. Yakobson & V.L. Auslender, *Solid State Ionics*. 1989, 36, 1 [3] A. P. Voronin, V. A. Neronov, V. V. Boldyrev, T. F. Melekhova, V. L. Auslender, V. V. Aleksandrov, N. Z. Lyakhov, V. A. Polyakov & M. A. Savinkina, *Soviet Powder Metallurgy and Metal Ceramics*. 1982, 21, 632 [4] V.L. Auslender, I.G. Bochkarev, V.V. Boldyrev, N.Z. Lyakhov & A.P. Voronin, *Solid State Ionics*. 1997, 101-103, 489

Keywords: functional ceramics, radiation-thermal synthesis, synchrotron radiation, X-ray structural and phase analysis

Pushing the limits of structure determination using SR-PXRD and Rietveld/MEM

Casper Andersen^a, Martin Bremholm^a, Peter Vennestrøm^b, Lars Lundegaard^b, Anders Blichfeld^a & Bo Iversen^a

^aAarhus University, Denmark, e-mail: cwa@inano.au.dk
^bHaldor Topsøe, Kgs. Lyngby, Denmark

Efficient elimination of environmentally harmful gaseous NO_x compounds from automotive diesel emission remains a challenging task. State-of-the-art zeolites with the chabazite framework containing catalytically active Cu²⁺ (Cu-SSZ-13) have been commercialized as NO_x after-treatment catalysts in diesel-powered vehicles, due to its superior activity, selectivity, and durability.^[1] However, to meet current and future legislative demands, continuous improvement is of fundamental interest. Prerequisites for an in depth understanding and further improvements, are detailed complete structural models of the Cu-loaded catalyst. This may be achieved by the use of high resolution synchrotron powder X-ray diffraction (PXRD) and iterative Rietveld analysis and Maximum Entropy Method (MEM).

Since the content of Cu²⁺ is low, a protonated system (H-SSZ-13) and model system with monovalent Ag⁺ ions (Ag-SSZ-13) are also examined. The protonated and dehydrated H-SSZ-13 shows perfectly empty voids, i.e. no water residue or other non-framework species. The H-SSZ-13 structure is used as the initial model for the MEM calculations. For Ag-SSZ-13 MEM analysis clearly pinpoints the Ag⁺ ion as being located in the 6-ring shifted into the chabazite cage, consistent with the generally accepted site for Ag⁺ ions in chabazite and reveals the strength of the iterative Rietveld/MEM analysis. For the more challenging case of Cu-SSZ-13 it was still possible through careful analysis and reasoning to locate two separate positions for the Cu²⁺ in Cu-SSZ-13. The B site has been suggested by several other studies, but never confirmed experimentally.^[2]

This is the most complete structural description of zeolite SSZ-13 with stabilizing and catalytically active Cu²⁺ ions.^[3]

[1] F. Gao, E. D. Walter, E. M. Karp, *et al.*, *J. Catal.* 2013, 300, 20
[2] U. Deka, A. Juhin, E. A. Eilertsen, *et al.*, *J. Phys. Chem. C* 2012, 116, 4809 [3] C. W. Andersen, M. Bremholm, P. N. R. Vennestrøm, *et al.*, *Angew. Chem. Int. Edit.* 2014, submitted

Keywords: Zeolite structure, Electron density, Maximum Entropy Method

Rietveld refinement of new Ca₁₀M(VO₄)₇ (M = Li, Na, K) whitlockites

Akram Behrooz^a, Wojciech Paszkowicz^a, Boris Nazarenko^b & Alexei Shekhovtsov^b

^aInstitute of Physics, Polish Academy of Sciences, al. Lotnikow 32/46, PL-02-668 Warsaw, Poland, e-mail: behrooz@ifpan.edu.pl

^bInstitute for Single Crystals, NAS of Ukraine, Lenin Ave. 60, 61001, Kharkov, Ukraine

Doped vanadium-based whitlockite-type (space group R3c), materials are considered as being applicable in optoelectronics, e.g., for white-light emitting LEDs, as discussed in Refs. [1, 2]. Some of them have already been grown as high-quality single crystals [3]. Doping by a monovalent metal, M, consists in location of the M atoms at Ca(4) sites and leads to a modification of the basic whitlockite formula from Ca₃(VO₄)₂ to Ca₁₀M(VO₄)₇. Among the possible compounds with M standing for an alkali metal, formation of material with M = K has been already reported in [4]. Ca₁₀M(VO₄)₇ compounds are expected to exhibit non-linear optical characteristics and to be suitable for second-harmonic generation. In the present work, investigation of Ca₁₀M(VO₄)₇ (M = Li, Na, K) crystal structure of polycrystalline samples prepared from perfect Czochralski-growth single crystals is determined. Powder diffraction experiments were performed using a laboratory Panalytical XPERT MPD diffractometer equipped with a Ge monochromator and a strip detector. Phase analysis shows that the crystals are pure whitlockite-type phases. The lattice parameters a and c of the studied samples are 10.81450(7) and 38.0657(3) for M = Li, 10.81612(5) and 38.0295(2) for M = Na, and 10.82891(8) and 38.0131(3) for M = K. The study presents the data on the structure of the three compounds and a discussion of the structural properties on the basis of comparison with some other whitlockite-type materials.

[1] X. Wu, Y. Huang, H.J. Seo, *Ceram. Int.* 2001, 37, 2323 [2] L. Liu, R.-J. Xie, N. Hirotsaki, Y. Li, *J. Spectrosc. Dyn.* 2013, 3,10 [3] M.B. Kosmyna, B.P. Nazarenko, V.M. Puzikov, A.N. Shekhovtsov, *Acta Phys. Polon. A* 2013, 124, 1282 [4] H. Mueller Buschbaum, O. Schrandt, *Z. Naturforsch. B* 1996, 51, 473

Keywords: whitlockite, vanadate, structure refinement, Rietveld method

Phase transitions in γ -TiAl based alloys and ordering/disordering phenomena

Premysl Beran^a, Milan Heczko^b, Bedrich Smetana^c, Monika Zaludova^c & Tomas Kruml^b

^aNuclear Physics Institute, ASCR, Rez, Czech Republic, e-mail: pberan@ujf.cas.cz

^bCEITEC, Institute of Physics of Materials, ASCR, Brno, Czech Republic

^cVŠB–Technical University of Ostrava, Ostrava, Czech Republic

During the last decade research activities have been focused to the development of TiAl alloys with high niobium additions. These alloys with the baseline composition Ti–44Al–7Nb (at.%) show good combination of high creep strength, good ductility at room temperature, improved fatigue properties and excellent oxidation resistance. Niobium decreases the stacking fault energy in γ -TiAl, diminishes diffusion processes and modifies the structure of the oxidation layer. However, applications of TiAl alloys in general are hindered by relatively low room temperature ductility, poor fracture toughness and bad hot workability [1]. One of currently studied ways to improve deformability (plasticity) of advanced γ -TiAl-Nb alloys is via the microstructure control by complex heat treatment which can introduce ductile β phases.

We studied base alloy Ti–44Al–7Nb and we gradually doped it with Mo and/or C. To develop appropriate heat treatment it is necessary to construct temperature phase diagram. Combination of several analytical techniques (neutron diffraction, differential scanning calorimetry and electron microscopy) was used to determine phase stability in selected alloys. These alloys have a very complex phase structure where ordered and disordered phases can be present. At room temperature the high niobium content TiAl alloys are mostly formed by the ordered tetragonal γ -TiAl phase and small amount of ordered hexagonal α_2 -Ti₃Al phase or the ordered cubic β_0 -TiAl phase. Disordered hexagonal and bcc phases are present mostly at elevated temperatures.

For the structure characterization of these multiphase TiAl alloys we have adopted *in-situ* neutron diffraction technique with temperature which allows determined structure evolution and also possible ordering/disordering phenomena in α and β phases. In combination with DSC curves temperature phase diagram was constructed for studied alloys. More over new type of partially ordered α -Ti₃Al phase was found after α -transus temperature.

[1] Appel F., Oehring M., Wagner R., *Intermetallics*, 8 (2000), 1283.

Keywords: gamma TiAl, phase diagram, neutron diffraction

Accurate Charge Densities from Powder Diffraction

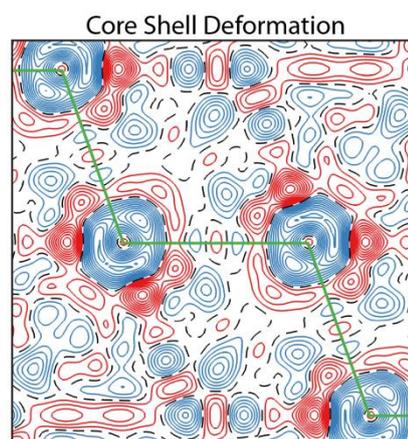
Niels Bindzus^a, Nanna Wahlberg^a, Ann-Christin Dippel^b, Jacob Becker^a & Bo B. Iversen^a

^aAarhus University, Denmark

^bPETRA III, DESY, Germany, e-mail: nielsb@chem.au.dk

Synchrotron powder X-ray diffraction (SPXRD) has in recent years advanced to a level, where extremely accurate information about the electron density distribution can be probed. Breaking with the conventional use of single-crystal diffraction in charge density (CD) studies, it can be advantageous to use SPRXD for simple, high-symmetry crystal structures owing to negligible extinction effects, minimal peak overlap, and the opportunity for collecting data on a single scale. Diamond is an excellent material for testing new methodologies, and the current study employs benchmark data measured to low d -spacing.^[1]

We scrutinize procedures for accurately recovering structure factors, F_{obs} , from the powder pattern. In addition to the traditional approaches, Rietveld and Le Bail, this includes the decomposition scheme recently proposed by Straasø *et al.*^[2] This novel method is structure-independent and excels in terms of simplicity. Its merit is that F_{obs} with negligible model bias are retrievable under certain experimental conditions. The present data fall into this category.



The performance of all three sets of F_{obs} is evaluated regarding their capability to determine the atomic displacement parameter and to estimate the CD by multipolar modelling and maximum entropy reconstruction. In accord with its huge success over the last decades, the Rietveld approach leads to superior results. In quantitative correspondence with theoretical predictions, they even reveal a contraction of the core shell that is inherently linked to the covalent bond

formation. The study of core polarization has emerged as a new frontier in chemical bonding studies, and reliable information about the innermost CD can be experimentally accessed by SPRXD for high-symmetry crystal systems.

[1] Bindzus *et al.*, *Acta Cryst. A*. 2014, 70, 39-48

[2] Straasø *et al.*, *J. Synchrotron Rad.* 2014, 21, 119-126

Keywords: Maximum Entropy Method, X-ray Charge Density, Core Shell Deformation

MS11_P128

Tuning Proton Conductivity in A Multifunctional Calcium Phosphonate Hybrid Framework

A. Cabeza^a, M. Bazaga-García^a, R.M.P. Colodrero^a, M. Papadaki^b, P. Olivera-Pastor^a, E.R. Losilla^a, L. León-Reina^a, D. Choquesillo-Lazarte^c, P. Garczarek^d, J. Zoi^d, M.A.G. Aranda^{a,e} & K.D. Demadis^b

^aUniversity of Malaga, Spain

^bUniversity of Crete, Greece

^cLaboratorio de Estudios Cristalográficos, IACT-CSIC, Spain

^dWroclaw University of Technology, Poland

^eCELLS-ALBA synchrotron, Spain

e-mail: aurelio@uma.es

Multi-chelating phosphonate ligands are organic linkers alternative to polycarboxylates and other ligands providing synthetic access to a number of thermally- and chemically-stable MOFs [1]. Metal phosphonates are amenable for accessing suitable and highly conducting materials both by tuning structural features and post-synthesis treatment [2,3]. For instance, proton conductivity values in the order of 10^{-2} S cm⁻¹ have been reported for several phosphonate-based compounds [4].

We report hereby the synthesis, structural characterization and proton conductivity of an open framework hybrid, $\text{Ca}_2[(\text{HO}_3\text{PC}_6\text{H}_3\text{COOH})_2]_2[(\text{HO}_3\text{PC}_6\text{H}_3(\text{COO})_2\text{H})(\text{H}_2\text{O})_2]_5\text{H}_2\text{O}$, that combines Ca^{2+} ions and the rigid polyfunctional 5-(dihydroxyphosphoryl)isophthalic acid ligand. This compound was obtained by slow crystallization at ambient conditions at pH ~3. Its complex pillared layered structure, solved by single crystal X-ray analysis, contains hydrophilic 1D channels filled with both water and acidic phosphonate and carboxylate groups creating a hydrogen-bonded network. Partial removal of the lattice water at 75 °C causes a monoclinic structural distortion but still retaining the initial conductivity

properties ($5.7 \cdot 10^{-4}$ S·cm⁻¹). Exposure of the sample to ammonia vapor from a concentrated aqueous solution led to major structural changes resulting in a new layered material containing seven NH₃ and sixteen H₂O molecules per formula. This solid exhibits enhanced conductivity, reaching $6.6 \cdot 10^{-3}$ S·cm⁻¹, as measured at 98 % RH and T = 24 °C. Activation energies were between 0.23 and 0.40 eV, typical of a Grothuss mechanism of proton conduction.

[1] *Metal phosphonate chemistry: From synthesis to applications*; Clearfield, A.; Demadis, K.D., Ed.; The Royal Society of Chemistry: London, 2012. [2] G.K.H. Shimizu, J.M. Taylor, S. Kim, *Science* 2013, 341, 354 [3] R.M.P. Colodrero, A. Cabeza, P. Olivera-Pastor, A. Infantes-Molina, E. Barouda, K. D. Demadis, and M. A. G. Aranda, *Chem. Eur. J.* 2009, 15, 6612. [4] R.M.P. Colodrero, P. Olivera-Pastor, E.R. Losilla, M.A.G. Aranda, L. Leon-Reina, M. Papadaki, A.C. McKinlay, R.E. Morris, K.D. Demadis, A. Cabeza, *Dalton Trans.* 2012, 41, 4045.

Keywords: MOF, inorganic-organic hybrids, proton conductivity, functional materials, phosphonate.

MS11_P129

Crystal structure of new phosphates $\text{Ca}_{9-x}\text{Pb}_x\text{Eu}(\text{PO}_4)_7$ from Rietveld refinement

Dina Deyneko^a, Sergey Stefanovich^a & Bogdan Lazoryak^a

^aLomonosov Moscow State University, Russia,

e-mail: deynekomsu@gmail.com

The phosphates $\text{Ca}_{9-x}\text{Pb}_x\text{Eu}(\text{PO}_4)_7$ were obtained by solid state reaction and were found to be isotopic with whitlockite-type $\beta\text{-Ca}_3(\text{PO}_4)_2$ (polar space group $R3c$). The crystal structure encloses 5 crystallographic sites different in size and oxygen coordination. The room temperature powder X-ray diffraction (PXRD) patterns of the $\text{Ca}_{9-x}\text{Pb}_x\text{Eu}(\text{PO}_4)_7$ were recorded on Bruker Smart X2S. PXRD data were collected over the 5°–85° 2 θ range with steps of 0.02°. To determine the lattice parameters, Le Bail decomposition was applied using the JANA2006 software [1]. Initially, the structure refined by the Rietveld method carried out starting from data [2]. Further, the population of the cation positions was refined. Phase analysis revealed that single-phase solid solutions exist up to $x = 1$. The JANA2006 program was ran using the pseudo-Voigt profile function to refined atomic coordinates and distances. The Ca/Eu splitting wasn't use in structure refinement. In connection with substitution scheme $(3\text{Ca}^{2+}) \rightarrow (2\text{Ln}^{3+} + \square)$ supplementary vacancies doesn't generated, so the M4 site is empty. After the last refinement, there was a good agreement between the observed and calculated patterns, and reasonable values

of isotropic temperature factors were found for all atoms. According to obtained data, Eu^{3+} ions preferentially occupy M1, M2 and M3 sites with calcium, contradicting previously published Mössbauer results [3]. M5 site is fully occupied by Ca^{2+} . Pb^{2+} ions primary enters into the M3 site and only then shares positions M1, M2 with calcium or Eu^{3+} ions. Second harmonic generation (SHG) tests evidenced higher nonlinear optical activity of lead-containing compositions, and it also reveals ferroelectric type phase transitions to centrosymmetric group $R3c \rightarrow R-3c$ between 500–600 °C. Structural mechanisms and dielectric features of phase transitions are strongly influenced by the exact distributions of guest atoms over the positions. This work was supported by RFBR, project no. 14-03-01100a.

[1] Dusek M., Petříček V., Wunschel M., Dinnebier R.E., Van Smaalen S., *J. Appl. Crystallogr.* 2001, 34, 398

[2] Benhamou R., Bessiere A., Wallez G. et al., *J. Solid State Chem.* 2009, 182, 2319

[3] Lazoryak B.I., Vitting B.N., Fabrichnyi P.B. et al., *Kristallografiya.* 1990, 35, 4, 1403

Keywords: whitlockite, polar structure, nonlinear optical activity, SHG, phase transition

MS11_P130

Structural modulations in potential multiferroic tetragonal tungsten bronze $\text{K}_x\text{Mn}_x\text{Fe}_{1-x}\text{F}_3$

[Christina Drathen](#)^a, [Kirill V. Yusenko](#)^b & [Serena Margadonna](#)^b

^aESRF, Grenoble, France, e-mail: drathen@esrf.fr

^bUniversity of Oslo, Oslo, Norway

Multiferroic materials showing coupling of the different order parameters (ferroelectric, ferromagnetic, ferroelastic) are interesting from a fundamental and technological point of view, e.g. for to the development of new storage technologies. However, the coexistence of (ferro)magnetism and ferroelectricity is considered a rare phenomenon. Whilst this may be true for perovskite oxides, where empty d -shells favor the off-centering of ions but counteract magnetism, this intrinsic limitation can be avoided by moving to different structure types, and/or away from oxides. An example of non-perovskite, non-oxide multiferroic systems are the tetragonal tungsten bronze fluorides $\text{K}_x\text{M}^{2+}_x\text{M}^{3+}_{1-x}\text{F}_3$ ($x = 0.4 - 0.6$), which show coexistence of electric and magnetic ordering¹.

Here we present our study on the crystal structure of the series $\text{K}_x\text{Mn}_x\text{Fe}_{1-x}\text{F}_3$ ($x = 0.4 - 0.55$) as a function of temperature using powder diffraction and DSC. KMnFeF_6 was reported as tetragonal $P4_2bc$ and orders ferrimagnetically below 148 K². Satellite reflections found in electron microscopy experiments were attributed to ferroelastic domains of tilted MF_6 octahedra and indexed with an orthorhombic supercell, where $a \approx 2\sqrt{2} a_{\text{TTB}}$, $b \approx \sqrt{2} a_{\text{TTB}}$ and $c \approx 2c_{\text{TTB}}$ ³. Yet the reported bulk powder diffraction measurements indicated only tetragonal symmetry³.

The high resolution of our powder diffraction data (beamline ID31, ESRF) reveals an orthorhombic distortion ($a \approx b \approx \sqrt{2} a_{\text{TTB}}$, $c \approx 2c_{\text{TTB}}$), which diminished when moving to the end members of the series ($x \rightarrow 0.4$ and $x \rightarrow 0.6$). Moreover, additional reflections suggest a monoclinic cell with $a \approx b \approx 2\sqrt{2} a_{\text{TTB}}$ and $c \approx 2c_{\text{TTB}}$. Although structurally subtle, this distortion may indicate a ferroelectric state, similar to K_xFeF_3 , where ferroelectricity is observed only in the orthorhombic phase. On heating, an anomaly in the c -axis lattice parameter accompanies a phase transition to centrosymmetric $P4_2/mbc$ around 350 K, marking the transition from ferroelectric to paraelectric state.

[1] Scott, J.F., Blinc, R., *J. Phys. Condens. Matter*, 2011, 23, 113202

[2] Banks E., Nakajima S. et al., *Acta Cryst.*, 1979, B35, 46

[3] Fabbri S., Montanari E. et al., *Chem. Mater.*, 2004, 16, 3007.

Keywords: multiferroics, tetragonal tungsten bronze, high resolution powder diffraction

MS11_P131

Supercritical Carbonization of Magnesium Silicate Clays

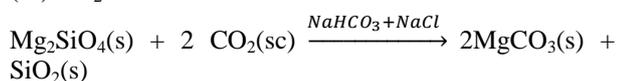
[Espen Eikeland](#)^a, [Christoffer Tyrsted](#)^b, [Anders Bank Blichfeld](#)^c
& [Bo B Iversen](#)^d

^aAarhus University, Denmark, eikeland@chem.au.dk

Due to the rise in atmospheric carbon dioxide levels, so-called carbon capture and sequestration has attracted attention as possible solution for recapturing and removing CO_2 from the atmosphere.^[1] One stable way of binding CO_2 is by forming carbonated solid compounds. This approach is of interest in several industries such as the cement industry which are responsible for approximately 5 % of the global anthropogenic CO_2 emission and subjected to considerable CO_2 -based expenses in the form of CO_2 quotas. Here the approach may be used in a cycle where CO_2 released during final calcination processes may be

captured and recirculated in clay mineral conversion earlier in the process.

In this project the studied carbonization reaction is production of magnesium carbonate (MgCO₃) directly from olivine (MgSiO₄). The project is conducted in collaboration with the Danish cement production company FLSmidth. The proposed hydrothermal model of the carbonization reaction of olivine in supercritical (sc) CO₂ is as follows:^[2]



In an attempt to optimize the carbonation reaction the effects of temperature, pressure, particle size as well as additive concentration were investigated. Complete conversion was achieved in several of the experiments, and it is shown that the reaction rate is highly dependent of the applied temperature, pressure and NaHCO₃ concentration. Using larger olivine particles (> 100 μm) resulted in conversion close to zero, while adding NaCl had little effect on the reaction rate. Scanning Electron Microscopy coupled with Energy Dispersive X-ray Spectroscopy revealed the formation of amorphous silica particles and MgCO₃ crystals with a size distribution from 1 - 4 μm.

-
- [1] Zevenhoven, R., J. Fagerlund, and J.K. Songok, *Greenhouse Gases-Science and Technology*, 2011. 1(1): p. 48-57
[2] McKelvy, M., et al., 2006: Arizona State University

Keywords: Carbonization, CO₂ emission, Magnesium Silicate

MS11_P132

Crystalline phase analysis of sintered ore by X-ray diffraction / Rietveld refinement

D. Fujimura^a, T. Ashahi^a, A. Ohbuchi^b, T. Konya^b, Y. Koike^a
& T. Nakamura^a

^aMeiji University, Kawasaki Japan
^bRigaku Corporation, Tokyo, Japan
e-mail : ce34033@meiji.ac.jp

In recent years, sintered ore has made up a growing proportion of a blast-furnace feedstock; because of the depletion of high grade iron ore.[1] The iron making process needs an enormous energy, and exhausts a large quantities of carbon dioxide (carbon dioxide emission from this process is top in the manufacturing industries). Therefore, at present, sintered ore has been high-performance and widely analyzed. Its composition is one of the most effective parameter to understand

properties of it. In this study, crystalline phase and amorphous phase in sintered ore were analyzed using powder X-ray diffraction / Rietveld refinement combined with internal standard method. JSS851-2 and JSS851-5 certified reference materials of sintered ore were analyzed using X-ray diffractometer Rigaku RINT-2500 TTR-III, which was operated at 50 kV and 300 mA. Bragg-Brentano focusing geometry was used, and data for Rietveld refinement were recorded in the 17 – 76° 2θ range, with 2θ steps of 0.01° (counting time was set for 3 or 4 s each step). Eskolaite (Cr₂O₃) powder was used as internal standard material. Major crystalline phases including hematite (Fe₂O₃), magnetite (Fe₃O₄), SFCA (Ca_{2.8}Fe_{8.7}Al_{1.2}Si_{0.8}O₂₀) and calcium silicate (CaSiO₄) were identified, and their quantitative analysis was carried out by Rietveld refinement using PDXL software. The analytical values of SFCA and calcium silicate can't validate by other crystalline analysis; because there have no standard materials. Therefore, element concentration was calculated from the concentrations of 5 phases with Rietveld method and compared with certified elemental values to validate the quantitative values obtained by Rietveld refinement. The value of Fe²⁺ was calculated from analytical value of magnetite. The calculated values accorded with certified values in the range of 10% errors. Therefore, it may be said that results of Rietveld refinement is with high accuracy.

-
- [1] L.X. Hsieh, J.A. Whiteman: *ISIJ Int.*, 1989, 29, 625.

Keywords: sintered ore, X-ray diffraction, Rietveld refinement

MS11_P133

Long Bis(pyrazolates) Meet Transition Metals: Structure, Stability and Adsorption of MOFs Featuring Large Parallel Channels

Simona Galli^a, Angelo Maspero^a, Carlotta Giacobbe^a,
Giovanni Palmisano^a, Norberto Masciocchi^a, Angiolina
Comotti^b, Irene Bassanetti^b & Piero Sozzani^b

^aUniversity of Insubria, Italy, e-mail: simona.galli@uninsubria.it
^bUniversity of Milano Bicocca, Italy

Metal-organic frameworks (MOFs) represent a consolidated research line in numerous disciplines, from chemistry to physics, materials science, biology and even pharmacology. As a matter of fact, the smart combination of tailored structural aspects and key functional properties renders MOFs potentially suitable

for technologically advanced applications. As shown also by our work [1-3], polyazolato-based MOFs appear particularly promising, because they typically juxtapose, to appealing structures and functions, high thermal stability and chemical inertness.

Along this research line, the present contribution focuses upon a family of bis(pyrazolato)-based MOFs isolated by coupling the long and rigid spacer 1,4-bis(1*H*-pyrazol-4-ylethynyl)benzene (H₂BPEB) to the transition metal ions Zn(II), Ni(II) and Fe(III) [4]. As established by state-of-the-art XRPD structure determination methods applied to *laboratory* data, the rod-like ligand connects the metallic nodes to fabricate porous 3-D networks containing 1-D pervious channels. The combination of thermal analyses and variable-temperature XRPD demonstrated the remarkable thermal robustness of the three materials, which are stable *in air* at least up to 415 °C, and the flexibility of the Zn(II)- and Ni(II)-based frameworks. Specific experiments permitted to test the chemical stability of the three species toward water as well as aqueous acidic and basic solutions, the Ni(II) derivative being stable and hydrophobic in all the conditions essayed. N₂ adsorption measurements at 77 K allowed to estimate promising Langmuir specific surface areas, peaking at *ca.* 2400 m²/g in [Ni(BPEB)]. Remarkably, adsorption experiments with CO₂ revealed that up to 40 % wt is adsorbed by the Fe(III) derivative under the mild conditions of 298 K and 10 bar, surpassing renown MOFs of comparable specific surface area. Moreover, at room temperature and at a moderate pressure, [Fe₂(BPEB)₃] also shows CH₄ uptake values comparable to those of highly performing MOFs.

Financial support by Fondazione Cariplo is acknowledged (Project 2011-0289).

[1] Colombo, V., Montoro, C., Maspero, A., Palmisano, G., Masciocchi, N., Galli, S., Barea, E., Navarro, J.A.R. *J. Am. Chem. Soc.* 2012, 134, 12830

[2] Galli S., Masciocchi N., Colombo V., Maspero A., Palmisano G., López-Garzón F.J., Domingo-García M., Fernández-Morales I., Barea E., Navarro J.A.R., *Chem. Mater.*, 2010, 22, 1664

[3] Masciocchi N., Galli S., Colombo V., Maspero A., Palmisano G., Seyyedi B., Lamberti C., Bordiga S., *J. Am. Chem. Soc.*, 2010, 132, 7902

[4] Galli S., Maspero A., Giacobbe C., Masciocchi N., Palmisano G., Nardo L., Comotti A., Bassanetti I., Sozzani P. *J. Am. Chem. Soc.*, 2014, submitted.

Keywords: X-ray powder diffraction, Metal-organic frameworks, Nitrogen-donor ligands, Thermal stability, Carbon dioxide adsorption.

MS11_P134

Multi-scale Powder Diffraction Investigation of Polymeric Spin-Crossover Materials

Philippe Guionneau^a, Arnaud Grosjean^a, Nathalie Daro^a,
Philippe Négrier^b, Pierre Bordet^c, Denise Mondieig^b, Eric
Lebraud^a, Stanislav Péchev^a & Jean-François Létard^a

^a CNRS, Univ. Bordeaux, ICMCB, Pessac, France

^bUniv. Bordeaux, LOMA, Talence, France ^cInstitut Néel CNRS/UJF
UPR294025, Grenoble, France.
guionneau@icmcb-bordeaux.cnrs.fr

The **spin-crossover** phenomenon (SCO) is a fascinating field that potentially concerns any material containing a (d4–d7) transition metal complex finding therefore an echo in as diverse research fields as chemistry, physics, biology and geology. Particularly, molecular and coordination-polymers SCO solids are thoroughly investigated since their bistability promises new routes towards a large panel of potential applications including smart pigments, optical switches or memory devices. Notwithstanding these motivating applicative targets, numerous fundamental aspects of SCO are still debated. Among them, the investigation of the **structure–property relationships** is unfailingly at the heart of the SCO research field.[1]

Powder diffraction methods are probably in a significant phase of development pushing the frontiers of investigations, in particular thanks to the progress in X-ray diffraction techniques. For instance, after a few decades of trials and failures, we have been recently able to determine the **crystal structures** of some **polymeric SCO compounds** using laboratory X-ray powder diffraction [2, 3]. These results have revealed unusual structural features in SCO materials, allowing a re-interpretation of the physical properties. In addition, powder diffraction has also allowed proposing a **multi-scale description** of the structural modifications associated to the SCO, from the atomic positions to **microstructures** including the coherent domain morphologies. For example, this approach has given a first insight into the notion of structural fatigability in polymeric SCO materials.[3] It has also opened the examination of the influence of the grain sizes on the structural and physical properties.

After an introduction to the SCO phenomenon and the role of **crystallography** within this field, we will present recent results that illustrate the paramount advantages offered by the use of powder diffraction in this research field. As a general interest, the approach developed here may probably be extended to **many other research fields** related to organic or inorganic materials showing phase transitions under a stimulus.

[1] P. Guionneau, *Dalton Trans.*, 2014, 43, 382-393.

- [2] A. Grosjean et al., *Eur. J. Inorg. Chem.*, 2013, 796-802.
[3] A. Grosjean, *PhD thesis*, Univ. Bordeaux, 2013.

Keywords: crystallography, spin-crossover, molecular material, powder diffraction, X-ray, microstructures, phase transition, iron

MS11_P135

Functionally graded multilayer for withstanding indentations and inhibition of hard particle embedding into the surface

Zdenek Pala^a, Kamil Kolarik^a, Radek Musalek^b, Jiri Kyncl^a & Libor Beranek^a

^aCzech Technical University in Prague, Czech Republic,
zdenek.pala@fff.cvut.cz, kamil.kolarik@fff.cvut.cz, jiri.kyncl@fs.cvut.cz,
libor.beranek@fs.cvut.cz

^bInstitute of plasma physics, Czech Republic, musalek@ipp.cas.cz

Processes when a large amount of hard particles such as alumina, zirconia and silica are pressed together represent a challenge not only for dies, where scratching took place, but also for punches with occurrence of multiple indentations. The damage of punches' due to the indentations can even lead to substantial embedding of the hard particles into the surface and, ultimately, the surface obtains a character of stickiness and must be repeatedly mechanically cleaned by e.g. brushing.

A multilayer consisting of three different layers, which limit the above described phenomena, was suggested and successfully tested during alumina-silica object pressing. The multilayer was created onto 56 HRC tempered hot work tool steel grade X40CrMoV5-1 that stands out by its high level toughness and dimensional stability. The novel multilayer consisted of nitrided layer, chromium nitride PVD coating and amorphous hydrogenated carbon diamond-like coating [1]. Optimization of the multilayer structure and properties was ensured by (i) XRD analyses of phase composition and residual stresses and by (ii) observations of microstructure and chemical composition on SEM after each stage of multilayer built-up. Residual stresses in nitride layer were determined by conventional single hkl diffraction experiment, but residual stresses in CrN were obtained by measuring several hkl reflections [2] and the resulting macroscopic stress tensor determined by method proposed by Winholtz and Cohen [3].

The optimized multilayer movement in the die was much smoother and it exhibited superb resistance to particle deadlock in the surface. Moreover, the punches' brushing could have been bypassed altogether and the

quality of the alumina-silica surface after pressing was considerably improved.

-
- [1] A. Grill, *Diamond and Related Materials*, 1999, 8, 428-434.
[2] U. Welzel, J. Ligot, P. Lamparter, A. C. Vermeulen and E. J. Mittemeijer, *J. Appl. Cryst.*, 2005, 38, 1-25
[3] R.A. Winholtz, J.B. Cohen, *Aust. J. Phys.*, 1988, 41, 189-199.

Keywords: FGM, multilayer, punch surface, nitriding, CrN, DLC, residual stresses.

MS11_P136

Continuous hydrothermal flow synthesis and characterization of SnO₂ nanoparticles - control of size and morphology

Henriette Ravn Larsen^a, Aref Mamakhel^a, Martin Søndergaard^a & Bo B. Iversen^a

^aCenter for Materials Crystallography, Department of Chemistry and iNANO, Aarhus University, Denmark, e-mail: henriette.ravn.larsen@post.au.dk

The development of materials for effective energy storage is becoming increasingly important as the performance of batteries has to meet the high energy demands of modern electronic devices.

SnO₂ is of great interest as a promising anode material for sodium ion batteries and the already existing effective, safe and lightweight lithium ion batteries. Since the properties of metal oxide materials such as SnO₂ greatly depend on the size and the morphology of the SnO₂ nanoparticles, it is crucial to be able to control these particle characteristics.

In this study SnO₂ nanoparticles are synthesized using a continuous flow supercritical system, which has proven to be a very promising method for controlling the size and the size distribution of nanoparticles [1]. The gel used as precursor is made from aqueous solutions of SnCl₄·5H₂O and NaOH.

A systematic study on the particle size and morphology dependence on different synthesis conditions, such as temperature, pH and concentration, is carried out.

The synthesized nanoparticles are characterized using Powder X-ray Diffraction (PXRD), Transmission Electron Microscopy (TEM) and the Brunauer-Emmett-Teller (BET) method.

Among other things, it is observed that the particle size decreases with decreasing synthesis temperature. Furthermore, as shown in a previous *in situ* study on SnO₂ [2], both a tetragonal and an orthorhombic crystal structure may be present depending on the synthesis conditions.

Overall, the SnO₂ particle characteristics can successfully be controlled by varying the synthesis conditions.

[1] Supercritical Propanol–Water Synthesis and Comprehensive Size Characterisation of Highly Crystalline anatase TiO₂ Nanoparticles, Peter Hald, Jacob Becker, Martin Bremholm, Jan S. Pedersen, Jacques Chevallier, Steen B. Iversen, Bo B. Iversen, *Journal of Solid State Chemistry*, 2006, 179, 2674–2680.

[2] Revealing the Mechanisms behind SnO₂ Nanoparticle Formation and Growth during Hydrothermal Synthesis: An In Situ Total Scattering Study, Kirsten M. Ø. Jensen, Mogens Christensen, Pavol Juhas, Christoffer Tyrsted, Espen D. Bøjesen, Nina Lock, Simon J. L. Billinge, and Bo B. Iversen, *Journal of the American Chemical Society*, 2012, 134, 6785–6792.

Keywords: SnO₂, battery material, continuous flow reactor, supercritical synthesis, nanoparticles, particle size, morphology

MS11_P137

Cation Distribution in (Y_{1-x}Eu_x)₂O₃ Luminescent Materials

Mika Lastusaari^{a,b}, Hermi F. Brito^c, José M. Carvalho^c, Salla Hakkola^a, Jiang Kai^d, Tero Laihinén^{a,e}, Cássio C.S. Pedroso^c, Lucas C.V. Rodrigues^{a,c} & Jorma Hölsä^{a,c}

^aUniversity of Turku, Department of Chemistry, FI-20014 Turku, Finland

^bTurku University Centre for Materials and Surfaces (MatSurf), Turku, Finland

^cUniversidade de São Paulo, Instituto de Química, São Paulo-SP, Brazil

^dPontifícia Universidade Católica do Rio de Janeiro, Departamento de Química Rio de Janeiro-RJ, Brazil

^eUniversity of Turku Graduate School (UTUGS), Doctoral Programme in Physical and Chemical Sciences, Turku, Finland
e-mail: miklas@utu.fi

Eu³⁺ doped rare earth oxides, R₂O₃:Eu³⁺ (R: La, Gd, Y, Lu, Sc), especially Y₂O₃:Eu³⁺, are efficient luminescent materials widely used in practical applications as red emitters [1]. The cubic C-type structure of Y₂O₃ with the space group Ia $\bar{3}$ (No. 206) has two cation sites (symmetries C₂ and S₆). A considerable part of the input energy may be lost to the yellowish emission between 590 and 600 nm, which originates from Eu³⁺ in the S₆ site [2,3]. In this work, the distribution of Eu³⁺ between the two sites in (Y_{1-x}Eu_x)₂O₃ (nominal x: 0–0.8; step 0.2) was investigated with X-ray powder diffraction data collected at room temperature at the beamline XPD of the LNLS synchrotron (CNPEM, Campinas, Brazil). The data was analyzed using Rietveld refinements [4] with the FullProf program [5].

The unit cell axis length increases nearly linearly with increasing actual Eu³⁺ content (Fig.) obtained from the Rietveld refinements. No broadening of the reflections was observed suggesting complete solid solubility in the system. The site occupancies indicate that the relative

content of Eu³⁺ is higher in the C₂ than the S₆ site. Emission from Eu³⁺ in the S₆ site is thus a minor problem below 10 % Eu³⁺ concentration (to be verified with luminescence studies).

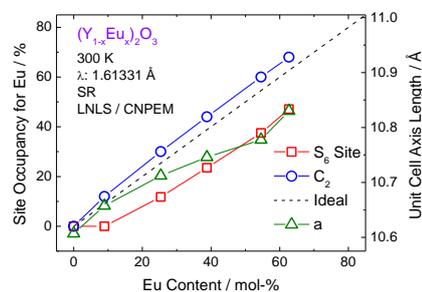


Fig. Site occupancy for Eu³⁺ in the two cation sites and the unit cell axis length for the (Y_{1-x}Eu_x)₂O₃ materials (esd's: smaller than the symbols).

[1] Shionoya, S. and Yen, W.M. (eds.), *Phosphor Handbook*, CRC Press, Boca Raton FL, USA, 1998. [2] Karbowski, M., Zych, E. and Hölsä, J., *J. Phys. Condens. Matter*, 2003, 15, 2169. [3] Antic-Fidancev, E., Hölsä, J. and Lastusaari, M., *J. Phys. Condens. Matter*, 2003, 15, 863. [4] Rietveld, H.M., *J. Appl. Cryst.*, 1969, 2, 65. [5] Rodriguez-Carvajal, J., 2012, *FullProf.2k (Version 5.30 - Mar2012)*, Laboratoire Leon Brillouin (CEA-CNRS), Gif-sur-Yvette, France, unpublished.

Keywords: Y₂O₃, Eu₂O₃, yttrium, europium, luminescence, Rietveld analysis, synchrotron, site distribution

X-Ray Diffraction facilities at the Institute of Condensed Matter Chemistry of Bordeaux

[Eric Lebraud](#), [Stanislav Péchev](#) & [Philippe Guionneau](#)

CNRS, University of Bordeaux, ICMCB, Pessac, France.
lebraud@icmcb-bordeaux.cnrs.fr

The laboratory ICMCB is located in Bordeaux, south west part of France, and mainly works on Solid State Chemistry, Material Science and Molecular Science. Its activities focus on four major sectors related to energy, functional materials, nano materials, environment and sustainable development. Two hundred and fifty researchers and staffs are working in seven major research groups and in twenty shared facilities. Among them, the **X-ray diffraction** center represents a key-stone for the investigation of materials.

The ICMCB X-ray diffraction centre is one of the largest French diffraction centre with not less than **eleven diffractometers** in the same place and dedicated to service. Two of them are design for single-crystals studies and nine are used for powder samples. Every year around 8000-9000 powder diffractograms are recorded.

The X-ray diffraction facilities currently **include powder diffraction at high temperature** (up to 1800K) and **low temperature** (down to 6K), single-crystals diffraction at low temperature (down to 80 K) and under various constraints (pressure, light) as well as the investigation of thin films and hygroscopic compounds. Optical microscopy, structural data bases and expertise in sample preparation are also provided, including capillaries or nano-powders. In addition, the X-ray centre benefits from the expertise of all crystallographers within the ICMCB teams allowing to survey a panel of material fields going from metallurgy to batteries, molecular materials and nano-crystals.

The X-ray diffraction centre develops a lot of collaborations with other academic laboratories and industrial partners providing a professional and efficient service in structural analysis **from simple phase identification to *ab initio* structural determination**.

Our **X-ray centre is open to any academic or industrial partners upon request**. The detailed technical and practical information will be presented and discussed on the poster.

Keywords: crystallography, powder diffraction, single crystals, X-rays, diffractometers, phase transition, variable temperature,

LiM(BH₄)₃Cl (M = La, Ce or Gd) – New lithium ion conductors

[Morten B. Ley](#)^a, [Raphaël Janot](#)^b, [Yaroslav Filinchuk](#)^c & [Torben R. Jensen](#)^a

^aCenter for Materials Crystallography (CMC), Interdisciplinary Nanoscience Center (iNANO) and Department of Chemistry, University of Aarhus, Langelandsgade 140, DK-8000 Århus C, Denmark.

^bLaboratoire de Réactivité et Chimie des Solides, UMR 6007 CNRS, Université de Picardie - Jules Verne, Amiens Cedex, France.

^cInstitute of Condensed Matter and Nanosciences, Université Catholique de Louvain, Place L. Pasteur 1, B-1348, Louvain-la-Neuve, Belgium.
Email: ley@inano.au.dk

Storage of renewable energy is essential in order to create a new sustainable energy economy e.g. directly as electricity in a lithium-ion battery or indirectly as hydrogen in a solid state metal hydride.¹ Lithium-ion batteries are rechargeable but have moderate life time and limited energy storage capacity. Metal borohydrides can store considerable amounts of energy as hydrogen in the solid state, but tend to exhibit poor thermodynamic and kinetic properties. Recently, we discovered a system of novel rare earth metal borohydrides with composition LiM(BH₄)₃Cl (M = La, Ce, Gd).^{2,3}

The structural determination of the new compounds was only possible by combination of powder X-ray diffraction, powder neutron diffraction and DFT calculations. Three structural models were considered for the structure, each with a unique lithium position within the structure. Careful analysis of the results from the three techniques resulted in a structural model agreeing with the high lithium conductivity ($\sigma \sim 1 \times 10^{-4} \text{ S}\cdot\text{cm}^{-1}$) of the compounds. Mechano-chemical synthesis from the corresponding rare earth metal chlorides (MCl₃, M = La, Ce, Gd) and lithium borohydride (LiBH₄) is the easiest production option. Unfortunately, this method inevitably co-produces none-conducting lithium chloride (LiCl). A battery assembled with LiGd(BH₄)₃Cl as solid state electrolyte have electrochemical activity. However, the assembled battery suffers from fast capacity loss due to large interfacial resistance most likely due to reduction of the cathode material by borohydride species.

[1] M. Fichtner, *J. Alloys Compd.*, 2011, 509, 529. [2] M. B. Ley *et al.*, *Chem. Mater.*, 2012, 24, 1654. [3] M. B. Ley *et al.*, *J. Phys. Chem. C*, 2012, 116, 21267.

Keywords: Solid state electrolyte, Metal borohydride, Solid state battery

Amine Templated Two Dimensional Tin Sulfides

Nina Lock^a, Mette Ø. Filso^a, Mogens Christensen^a & Bo B. Iversen^a

^aAarhus University, 8000 Aarhus C, Denmark

Tin-sulfur chemistry is highly diverse. Both elements are stable in various oxidation states, which in combination with their flexible bond geometries result in compounds with distinct structures and properties. An interesting class of tin sulfides is amine templated thiostannates consisting of negatively charged tin sulfide layers with positively charged molecules sandwiched in-between.^[1] The compounds are semiconducting with band gaps around 2.8-3.0 eV, and they emit a broad band of orange/red light, making them promising for use in optical devices.^[2,3]

We are presenting a detailed study on a novel amine-templated two-dimensional tin sulfide. The fundamental building units are Sn₃S₄ broken cube clusters connected by double sulfur bridges to form (Sn₃S₇)_n honeycomb hexagonal layers. Interestingly, the templating amine undergoes an intramolecular reaction during the synthesis to form charge stabilizing imidazolate ions which connect the SnS-layers in solid state. Multi-temperature powder diffraction data collected at SPring-8 on the orthorhombic compound reveal highly anisotropic thermal expansion of the compound. The lattice shows non-linear thermal expansion along the *b*- and *c*- axis resulting in a local maximum in unit cell volume at 300 K and zero-thermal expansion between 300 and 350 K. All three unit cell axes increase linearly with temperature in the range 150-225 K with linear coefficients of thermal expansion at 150 K along the *a*-, *b*-, and *c*-axis, $\alpha_l = dl/(dT \cdot l_{150\text{ K}})$, of $19.0(6) \cdot 10^{-6}$, $8.4(7) \cdot 10^{-6}$, and $52.2(6) \cdot 10^{-6} \text{ K}^{-1}$, respectively. The layers stack along the *c*-axis and the large expansion along *c* can be ascribed to the weak bonding between the SnS-sheets. The in-plane anisotropy is coupled to different flexibility of two crystallographically distinct double sulfur bridges in the SnS-layers.

[1] T. Jiang, A. Lough, G. A. Ozin, R. L. Bedard and R. Broach, *J. Mater. Chem.* 1998, 8, 721-732. [2] T. Jiang, G. A. Ozin and R. L. Bedard, *J. Mater. Chem.*, 1998, 8, 1641-1648. [3] N. Pienack, D. Schinkel, A. Puls, M.-E. Ordolff, H. Lühmann, C. Näther and W. Bensch, *Z. Naturforsch.*, 2012, 67b, 1098 – 1106.

Keywords: 2D materials, organic-inorganic hybrids, anisotropic thermal expansion

Short lead(II) alkanoates: from weakly fluorescent crystals to strong phosphorescent and varied vitreous phases

Francisco J. Martínez-Casado^a, Miguel Ramos-Riesco^b, José A. Rodríguez-Cheda^b, Fabio Cucinotta^c, Alejandro Fernández-Martínez^d, Leoncio Garrido^e, Emilio Matesanz^b & Leonardo Marchese^c

^aMAX IV Laboratory, Lund University, Sweden, email: francisco.martinez@maxlab.lu.se

^bUniversidad Complutense de Madrid, Spain.

^cUniversità del Piemonte Orientale, Italy.

^dIS Terre, Maison des Geosciences, France.

^eConsejo Superior de Investigaciones Científicas (ICTP-CSIC), Spain.

Most of the metal soaps (or alkanoates) are 2D-coordination polymers in the crystal phase, showing a bilayered arrangement with metal and carboxylate ionic layer and all-trans alkyl chains lipidic alternating layers. This structure makes possible that these salts may present polymorphism and *polymesomorphism* (that is, several mesophases) from the crystal to the melt. Depending on the metallic ion, they may present interesting properties. Thus, weak luminescence was detected in lead(II) soaps [1], although their thermal behavior has been studied for years [2-4]. This feature pointed to the possibility of tuning or enhancing the luminescence of lead compounds by getting different phases with different disorders, with the aim of changing the atomic distances and modifying the environment of the electron orbitals of Pb.

Short lead(II) alkanoates, from propionate to heptanoate have been studied in this work. They show a very intricate and reversible thermal behavior, presenting several mesophases and also three different glass states (regular or amorphous, liquid crystal and rotator glasses) with different degrees of ordering, besides the crystal phases, depending on the alkyl chain length. A thorough thermal study was carried out in order to study the different phases and to analyze the thermodynamic and kinetic parameters of the different phases and glasses.

The crystal structure was solved by powder x-ray diffraction for all the compounds, showing a similar arrangement in the 2D-stacking of the molecules. The PDF analysis, from diffraction data and carried out in all the phases, allowed to determine the local structure of the glasses and to compare them with the ones of the crystal phases, showing very important changes in the short distances. This allows to establish a direct relationship between structure and optical properties. Thus, the luminescent properties in the crystal phase are remarkably enhanced in the glass states, passing from weak fluorescence at low temperature to strong

phosphorescence at low and room temperature, respectively.

[1] Burrows, H. D. *Mater. Lett.* 1988, 6(5-6), 191. [2] Bazuin, C. G.; Guillon, D.; Skoulios, A.; Amorim da Costa, A. M.; Burrows, H. D.; Geraldes, C. F. G. C.; Teixeira-Dias, J. J. C.; Blackmore, E.; Tiddy, G. J. T. *Liq. Cryst.* 1988, 3(12), 1655. [3] Martínez Casado, F. J.; García Pérez, M. V.; Redondo Yélamos, M. I.; Cheda, J. A. R.; Sánchez Arenas, A.; López de Andrés, S.; García-Barriocanal, J.; Rivera, A.; León, C.; Santamaría, J. *J. Phys. Chem. C* 2007, 111(18), 6826. [4] Martínez Casado, F. J.; Ramos Riesco M.; Sánchez Arenas, A.; García Pérez, M. V.; Redondo, M. I.; López-Andrés, S.; Garrido, L.; Cheda, J. A. R., *J. Phys. Chem. B* 2008, 112(51), 16601.

Keywords: Lead(II) alkanoates, crystal structure and glass phases, powder X-ray diffraction, PDF analysis, fluorescence, phosphorescence, DSC.

MS11_P142

Hydration performance of Ni-exchanged montmorillonite "Quantitative XRD analysis"

Ammar Marwa^a, Walid Oueslati^b, Abdessalem Ben Haj Amara^a & Hafsia Ben Rhaïem^a

^a UR 05/13-01 : Physique des Matériaux Lamellaires et Nanomatériaux Hybrides (PMLNMH), Faculté des Sciences de Bizerte, Zarzouna 7021, Tunisia.

^b Technical and Vocational Training Corporation; College of Electronics & Communications, General studies department, TV street, P.O.Box 2816 Jeddah 21461, Kingdom Of Saudi Arabia.
e-mail: walidoueslati@gmail.com

The present study focused characterizing the effect of humidifying/ drying cycles, performed "in situ" by varying the sequence orientation of the relative humidity rates (%RH), in the case of a natural montmorillonite (i.e. SWy-2) exchanged by Ni (II) cations. These aims were accomplished using the quantitative XRD investigation based on an indirect method consisting on the comparison of experimental 00l reflections with other calculated from structural models. This method allowed us to determine respectively, the relative layer types contribution, the interlamellar water molecules amount and diverse structural parameters along the c* axis such as position, organization of water molecule and exchangeable cation. The theoretical proposed models, used to fit experimental data, show that the heterogeneous hydration state is the dominated character detected all over studied cycles. By varying the RH value a modification in the main structure of the host materials appeared and a mixed layer structure (MLS) including different abundance of dehydrated (0W), mono-hydrated (1W), bi-hydrated (2W) and three- hydrated (3W) layer types are imposed. Moreover, a logic hydration hysteresis in the low and the high RH range

in both studied cases appears which can be explained by the water retention mechanism fluctuation and the hydration heterogeneities created within the smectite crystallite.

Keywords: SWy-2-Ni, humidifying/ drying, water retention, hydration heterogeneities, quantitative XRD analysis.

MS11_P143

Quantitative XRD investigation of the hydration properties of a dioctahedral smectite Ba²⁺ and Mg²⁺ exchanged: Effect of ionic radius and relative humidity

Ben Rhaïem Hafsia, Ammar Marwa, Oueslati Walid & Ben Haj Amara Abdessalem

UR05/13-01: Physique des Matériaux Lamellaires et Nano-Matériaux Hybrides (PMLNMH), Faculté des Sciences de Bizerte, Zarzouna 7021, Tunisia
benrhaïem_hafsia@yahoo.fr; ammar.marwa@gmail.com;
walidoueslati@gmail.com; abdessalem.bha@gmail.com

Clays and clay minerals are the most sensitive minerals in the soil (Tessier & Isambert 1978; Ben Rhaïem et al. 1987). These minerals are generally made up of layers with important lateral extension stacked along the normal to their plane to constitute particles which size is of the order of 2µm. Smectite is a crucial component used for elaboration of natural barriers in industrial wastes and wastewater treatment. This work focuses on examining effect of a continuous in-situ variation of the relative humidity rate (%RH) on the hydration properties of the Wyoming montmorillonite (SWy-2) which is a dioctahedral smectite. The study is carried out on samples which CEC (Cation Exchange Capacity) was saturated with Ba²⁺ and Mg²⁺ cations. These two cations are characterised by different ionic radius. The structural evolution during a drying-rewetting cycle was performed by means of XRD analysis. The variation of the %RH affects the water content within the interlamellar space and thus the structural parameters along the perpendicular to the layer plane. Thus this study was achieved on 00l reflections in order to understand the hydration state of samples when varying %RH. Quantitative XRD analysis was carried out using an indirect method based on the comparison of experimental to calculated 00l XRD patterns. The samples were labelled WWY-2-Ba and SWy-2-Mg respectively for samples Ba and mg exchanged. A qualitative examination of XRD profiles suggests an heterogeneity of the hydration state all over the cycle and for both cations. This was confirmed by quantitative interpretation. Indeed, the modelling of 00l

XRD reflexions involved several mixed-layered phases of dehydrated (0W), one-water (1W), two-water (2W) and three-water (3W) layers. On the other hand, the interlamellar space of SWy-2-Mg complexes exhibits more fluctuations and is characterized with an hysteresis behaviour during the drying-rewetting cycle.

Tessier D. & Isambert (1978). Proc. Cong. Clay Minerals and soil fertility improvement, Prague, 122-132.
Ben Rhaiem H.; Pons C. H. & Tessier D. (1987) Proc. Intern. Clay Conf. Denver, 1985, L. G. Schultz, H. Van olphen and F. A. Mumpton eds., The clay Mineral society, Bloomington, Indiana, 292-297.

Keywords: Smectite, ionic radius, humectation–desiccation cycle, relative humidity, interlayer water, heterogeneous, hysteresis

MS11_P144

Synthesis and characterization of ZnO nanoparticles obtained by the sol–gel method from $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$

Ben Rhaiem Hafsia, [Akkari Marwa](#) & Ben Haj Amara Abdessalem

UR05/13-01; PMLNMH: Physique des Matériaux Lamellaires et Nano-Matériaux Hybrides, Faculté des Sciences de Bizerte, Zarzouna 7021, Tunisia
benrhaiem_hafsia@yahoo.fr, akkari.maroi@gmail.com;
abdessalem.bha@gmail.com

This study aims at synthesizing zinc oxide nanopowders according to the sol–gel method from a methanol solution of zinc acetate dehydrate and methanol solution of KOH. Detailed structural and microstructural investigations were carried out using X-Ray Diffraction (XRD), High-Resolution Transmission Electron Microscopy (HRTEM) and Infrared spectroscopy (FTIR). XRD patterns examination indicates that the obtained nanoparticles are homogenous with (100), (002) and (101) reflections of hexagonal ZnO crystal structure. The ZnO particle sizes determined from HRTEM observations are situated in the 7 nm - 15 nm scale.

Keywords: ZnO nanoparticule, sol-gel, chemical synthesis

MS11_P145

Formation of Size-Controlled $\text{SrFe}_{12}\text{O}_{19}$ Nano-Particles by Hydrothermal Synthesis

[Anna Zink Mortensen](#)^a, [Cecilia Granados-Miralles](#)^b & [Mogens Christensen](#)^c

^a Department of Chemistry & iNANO, Center for Materials Crystallography, Aarhus University, Denmark, e-mail: annazn@chem.au.dk

Permanent magnets have great importance for many technological applications. Many of the permanent magnets used contains rare earth metals specially Nd, which is expensive and difficult to handle without irradiating the miners or damaging the nature. Strontium hexaferrite, $\text{SrFe}_{12}\text{O}_{19}$, can be an alternative to some of the rare-earth containing magnets used today. The compound is special because of its high theoretical coercivity. It forms nanocrystallites, which has a hexagonal platelet shape with a short dimensions along the c-axis compared to the ab-axis. A strong anisotropy gives a strong preferred magnetization direction along the c-axis. Because of its shape it should be possible to align the particles in the same direction and gets a high net magnetization. One of the challenges is getting single domain particles; otherwise the domains will cancel out each other. In order to do so the particle size need to be small.

Synthesis of nanocrystallites through a fast heating process has been investigated. Particle size and shape has been investigated as function of start concentration, Sr:Fe ratio, and reaction time. With very fast heating and short reaction time the resulting crystallites are nano sized and generally with small amounts of impurities.

The samples are analyzed by X-ray diffraction and a Rietveld Refinement is done to determine particle size. The magnetization is characterized using Vibrating Sample Magnetometer (VSM).

Keywords: Magnetic materials, nanoparticles, hydrothermal synthesis, hexaferrite

Elaboration and characterization of a Clay hybrid ($\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4\text{-LiCl}$) as a solid electrolyte for Lithium ion battery

Ben Rhaïem Hafsia, Jaafar Nouha & Ben Haj Amara Abdessalem

Department of Physics, UR05/13-01: Physique des Matériaux Lamellaires et Nanomatériaux Hybrides (PMLNMH), Faculty of Science of Bizerte, Zarzouna 7021, Tunisia
 benrhaïem_hafsia@yahoo.fr; nouhajaafar@yahoo.fr; abdessalem.bha@gmail.com

Hybrid Nacrite-LiCl was synthesized from a tunisian nacrite and labeled $[\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4\text{-LiCl}]$. This complex was functionalized in presence of acetone as an organic solvent at room temperature. The intercalation of Li^+ cations within the interlayer space of nacrite has remarkable influence on both structural and electrical properties. Quantitative X-ray diffraction (XRD) analysis allowed us to determine the structural parameters related to the intercalated entities in the interlamellar space and their position along the normal of the layers. The basal spacing values increase from 7.2 Å to 11.43 Å. Moreover, Infrared Spectroscopy (IR) indicates interactions between nacrite functional surface groups, intercalated ions and water molecules due to hydrogen bonds formed between the hydrated salt and the inner-surface hydroxyls of the mineral. The electrical properties of nacrite-LiCl were also investigated by means of electrochemical impedance spectroscopy (EIS). The experiments were performed within a large frequency range (10 Hz –13 MHz) and temperature (from ambient until 873K) including the phase transition temperature. The *dc* conductivity evolution is consistent with the universal Arrhenius law. The *dc* conductivity values vary from $28.6 \cdot 10^{-5} \Omega^{-1}\text{m}^{-1}$ at 508 K to $11.5 \cdot 10^{-2} \Omega^{-1}\text{m}^{-1}$ at 873 K. The activation energy ($E_{a(\text{dc})}$) is equal to 0.84 eV in the temperature range (508-668K) and to 0.82 eV in the temperature range (673-873K). This indicates that nacrite-LiCl behaves as a super-ionic conductor at high temperatures. A similar behavior is denoted at high frequency (1MHz) for the *ac* conductivity. The activation energy ($E_{a(\text{ac})}$) was found to be equal to 0.51 eV in the temperature range (508-668K) and 0.71 eV in the temperature range (673-873K). Thus, the ionic conduction mechanism proposed is related to the Li^+ cations mobility thermally activated. This phenomenon is consistent with *the hopping model*. The dielectric permittivity (ϵ') decreases whereas the dielectric losses (ϵ'') increases with increasing temperature. The thermogravimetric and the differential thermal analyses (TG/DTA) show, that the hybrid thermal decomposition of is reasonably consistent with the ionic conductivity measurements. We conclude that the hybridization of nacrite by incorporation of Li^+ ions, results in a

considerable enhancement of the electrochemical properties of the obtained hybrid. Finally, this innovative nacrite-LiCl hybrid exhibits high ionic conductivity at high temperature and low cost compound, thus, it can be used as a solid electrolyte for Li-ion batteries.

Keywords: layered clay nacrite; hybrid material; functionalization; lithium chloride; XRD; IR; TG/DTA; impedance spectroscopy ; ionic conduction ; Lithium ion battery

Influence of Strain on Structural and Magnetic Phase Transitions: Nanocrystalline versus Bulk Properties of $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$

Lucia Pagliari^a, Monica Dapiaggi^a, Ilenia Tredici^b, Tapan Chatterji^c, Tapati Sarkar^d & Michael Carpenter^e

^aUniversity of Milan, Italy
^bUniversity of Pavia, Italy
^cScience Division, Institut Laue-Langevin, Grenoble, France
^dUniversity of Uppsala, Sweden
^eUniversity of Cambridge, UK.
 e-mail:lucia.pagliari@unimi.it

Nanocrystallinity is widely known as the feature responsible for big changes in the physical properties of a material, because of the increased surface to volume ratio. Elastic properties, whose variations detect the occurrence of a phase transition, are one of those characteristics that can change when nanoscale is reached. The expectation is that the spontaneous strain, that usually accompanies phase transformations, is largely modified in nanocrystals. The study considered here is based on the evaluation of coupling between strain and phase transitions in nano and bulk $\text{La}_{0.5}\text{Ca}_{0.5}\text{MnO}_3$ (LCMO) samples.

LCMO has (nominally) $\text{Mn}^{3+}/\text{Mn}^{4+}=1:1$ charge ordering (CO) below 225 K, which is accompanied by the paramagnetic-ferromagnetic transition, followed by a change towards the antiferromagnetic state at 155 K [1-3], if the material is not nanometric [3,4]. Resonant Ultrasound Spectroscopy (RUS) is the technique used in order to study the elastic properties of this material, between 5 and 295 K, so to follow all its structural and magnetic changes. Different grain-sized LCMO powders have been synthesized [4] and sintered with High Pressure Field Applied Rapid Sintering [5]. The crystallite dimensions of these pellets have been characterized by means of XRPD line profile analysis and are 33.57, 42.16, 75.02 and 136.29 nm.

The result is dual: the elastic measurements show only the CO transition, although the magnetic state (detected by a SQUID magnetometer) varies in all the pellets at 260 K (and also at 120 K in the coarsest one), so strain is significantly coupled only with the CO order parameter; in nanocrystals the shear modulus variation is weaker and less defined than in the bulk sample, so the grain size influences the elastic properties, by reducing the strain coupling. These observations can be useful for LCMO applications: its properties can, indeed, be tailored by synthesized materials with a definite grain size.

-
- [1] P. Schiffer, A.P. Ramirez, W. Bao, S-W. Cheong, *Phys. Rev. Lett.* 1995, 75, 3336.
 [2] P.G. Radaelli, D.E. Cox, M. Marezio, S-W. Cheong, *Phys. Rev. B*, 1997, 55, 3015.
 [3] Z. Jiráček, E. Hadová, O. Kaman, K. Knížek, M. Maryško, E. Pollert, *Phys. Rev. B* 2010, 81, 024403.
 [4] T. Sarkar, B. Ghosh, A.K. Raychaudhuri, T. Chatterji, *Phys. Rev. B* 2008, 77, 235112.
 [5] F. Maglia, I.G. Tredici, U. Anselmi-Tamburini, *J. Eur. Ceram. Soc.* 2013, 33, 1045.

Keywords: strain, phase transitions, nanomaterial

MS11_P148

Lattice Parameters and Thermal Expansion of Polycrystalline GaN: An X-ray Diffraction Study in a Broad Temperature Range

W. Paszkowicz^a, R. Minikayev^a, P. Piszora^b, M. Knapp^c, C. Bähz^d & S. Podsiadlo^e

^a Institute of Physics, PAS, al. Lotników 32, 02-668 Warsaw, Poland, e-mail: paszk@ifpan.edu.pl

^b Adam Mickiewicz University, Faculty of Chemistry, Grunwaldzka 6, 60-870 Poznań, Poland

^c Karlsruhe Institute of Technology, Institute for Applied Materials-Energy Storage Systems, Karlsruhe, Germany

^d Institute of Ion Beam Physics and Materials Research, Helmholtz-Zentrum Dresden Rossendorf, D-01314 Dresden, Germany

^e Faculty of Chemistry, Warsaw University of Technology, ul. Noakowskiego 3, 00-664 Warsaw, Poland

Binary III-V nitrides and their solid solutions exhibit unique physical properties leading to applications as thin-film components in optoelectronic devices. Detailed knowledge of both, the crystal structure and its variation with temperature, provides a necessary basis for development of such devices. The existing data on thermal expansion of one of key binary nitrides, GaN, include those for polycrystalline material (determined mostly in limited temperature ranges) [1–3] and those for single crystalline GaN [4, 5]. In the present study, the measurements were undertaken for a pure polycrystalline gallium nitride with the aim of

determination of lattice parameters, nitrogen atomic position and thermal expansion in the range from a low (14 K) up to a high (1073 K) temperature. The measurements were carried out at a powder diffractometer at the B2 beamline at HASYLAB/DESY. A He cryostat and graphite heater with rotating capillary was applied in the low and high temperature ranges, respectively. The parallel-beam instrumental set up included a Ge (111) double monochromator and a curved on-site readable imaging plate. For sample mounting a thin-wall glass and quartz (0.3 mm in diameter) capillaries were applied. Structure refinements were performed using the Rietveld method. Smooth dependencies of lattice parameters on temperature were obtained. From these data, the temperature runs of thermal expansion coefficients are derived. The temperature dependencies of both, the lattice parameters and thermal expansion coefficients, are found to follow the trends previously reported for narrow temperature intervals.

-
- [1] E. Ejder, *phys. stat. sol. (a)* 1974, 23, K87 [2] A.U. Sheleg, V.A. Savastenko, *Vestsi Akad. Navuk BSSR*, 1976, 3, 126 [3] R.R. Reeber, K. Wang, *J. Mater. Res.* 2000, 15, 40 [4] M. Leszczynski, T. Suski, H. Teisseyre, P. Perlin, I. Grzegory, J. Jun, S. Porowski, T.D. Moustakas, *J. Appl. Phys.* 1994, 76, 4909 [5] C. Roder, S. Einfeldt, S. Figge, D. Hommel, *Phys. Rev. B* 2005, 72, 085218

Keywords: powder diffraction, thermal expansion, III-V nitrides

MS11_P149

Location of Ge and extraframework species in the zeolite ITQ-24

Ana B. Pinar^a, Lynne B. McCusker^a, Christian Baerlocher^a, Joel Schmidt^b, Mark E. Davis^b & Stacey I. Zones^c

^aLaboratory of Crystallography, ETH Zurich, Switzerland
^bDept. Chemical Engineering, CalTech, Pasadena CA, USA
^cChevron ETC, Richmond CA, USA
 e-mail: ana.pinar@mat.ethz.ch

The germanosilicate ITQ-24 was synthesized in fluoride medium using 1,3,5-triazolium benzene as the structure directing agent (SDA). To examine the finer details of this zeolite structure, Rietveld refinement was initiated in the space group *Cmmm* (highest possible symmetry) with the known **IWR** framework structure [1]. A difference electron density map revealed the location and conformation of the SDA at the intersection of the 10- and 12-ring channels quite clearly. The benzyl ring is oriented perpendicular to the *b* axis with all three imidazolium moieties on one side forming in a "T-shaped" arrangement. Ge atoms were

found to replace some of the Si in the double-4-ring (*d4r*) and in one of the single-4-rings (*s4r*) to yield average compositions of [4Si,4Ge] and [3Si,1Ge], respectively. The other *s4r* in the framework contains only Si. Refined T-O distances (T: Si or Ge) and T-O-T angles are consistent with this Ge distribution. Fluoride anions were found to occupy the center of the *d4r*, in agreement with the ¹⁹F NMR spectrum, which is dominated by a signal at -10 ppm with a weaker signal at -20 ppm. These have been assigned in the literature to F⁻ in [4Si,4Ge] and [7Si,1Ge] *d4r*'s, respectively [2]. However, in *Cmmm*, the geometry of the framework was strained. Therefore, an independent evaluation of the symmetry was performed by running the powder charge flipping algorithm implemented in *Superflip* [3]. The results suggested that at least two of the mirror planes were missing. However, refinements in *Cmm2*, *Cm2m* and *C222* all failed. Then *Pban*, the only subgroup of *Cmmm* with no mirror planes or 2-fold axes, was tried. With this symmetry, the bond distances and angles became much more reasonable. By applying several different crystallographic techniques to synchrotron powder diffraction data, the structure of as-synthesized ITQ-24 could be fully characterized.

[1] R. Castañeda, A. Corma, V. Fornes, F. Rey, J. Rius, *J. Am. Chem. Soc.* 2003, 125, 7820.

[2] T. Blasco, A. Corma, M.J. Diaz-Cabañas, F. Rey, J.A. Vidal-Montoya, C.M. Zicovich-Wilson, *J. Phys. Chem. B.* 2002, 106, 2634.

[3] L. Palatinus, G. Chapuis, *J. Appl. Crystallogr.* 2007, 40, 786-790

Keywords: zeolite ITQ-24, germanosilicate, Rietveld refinement, 1,3,5-triimidazolium benzene

MS11_P150

Hydrothermal *In* and *Ex Situ* PXRD Study of MSb₂O₄ (M = Mn, Fe, Co) Functional Materials

Martin Roelsgaard^a, Peter Nørby^a & Bo Brummerstedt Iversen^a

^aCenter for Materials Crystallography, Department of Chemistry and iNANO, Aarhus University, e-mail: m.roelsgaard@chem.au.dk

Development of new functional materials for energy storage and conversion are of technological and scientific interest as they might have performance characteristics in presently uncovered regions. The transition metal antimony(III) oxide compounds (MSb₂O₄, M = Mn, Fe, Co, Ni) have potential use in thermoelectric and battery applications [1] owing to an inherent structural cavity. Nanostructuring, *i.e.* control of particle size and morphology, is of interest for the

performance of such materials. The crystallographic structure of the metal antimony(III) oxides is well-known (space group: P4₂/*mbc*, no. 135, Schafarzikite mineral), but there are still some fundamental challenges that need to be addressed in order to increase the applicability of these compounds. In the conventional solid-state synthesis method relatively high temperatures (600 °C) are needed [1-2], and this results in impurities and poor control of morphology and particle size. Hydrothermal processing offers an environmentally benign synthetic route, and provides tools to gain control of the challenges mentioned above.

We present an *in* and *ex situ* powder X-ray diffraction (PXRD) study of a novel hydrothermal synthesis method of phase pure MSb₂O₄ (M = Mn, Fe, Co). The particle size, growth and morphology dependence on different synthesis conditions have been monitored in real time by *in situ* synchrotron PXRD. Furthermore, we show by Rietveld refined structural parameters from multi-temperature *ex situ* synchrotron PXRD and thermal analysis that the stability, *e.g.* decomposition temperature, of the compound is also highly dependent on synthesis conditions.

[1] Jibin, A. K.; Reddy, M. V.; Subba Rao, G. V.; Varadaraju, U. V.; Chowdari, B. V., *Electrochim. Acta.* 2012, 71, 227-232 [2] de Laune, B. P.; Greaves, Colin, *J. Solid State Chem.* 2012, 187, 225-230

Keywords: Schafarzikite, *In Situ* X-ray Diffraction, Growth, MSb₂O₄, Functional Materials, hydrothermal synthesis

MS11_P151

Enalapril maleate characterization in solid formulations

Juliana A. P. Sato^a & Fabio F. Ferreira^a

^aUniversidade Federal do ABC, Brazil, e-mail: juliana.sato@ufabc.edu.br

Enalapril Maleate is an antihypertensive drug currently being administered in tablet form. This is an angiotensin-converting enzyme inhibitor and is used in the treatment of cardiovascular diseases. It is known to exist in at least two polymorphic forms, exhibiting similar stabilities. Form I crystallizes in a monoclinic system¹ P2₁ while Form II has been identified as an orthorhombic crystal, space group P2₁2₁2₁.

Polymorphic forms of a drug substance can have different chemical and physical properties, including melting point, chemical reactivity, apparent solubility, dissolution rates, optical and mechanical properties,

vapor pressure, and density. Thus, polymorphism can affect the quality, safety, and efficacy of the drug product².

In this work we analyzed five tablets of enalapril maleate, two samples of active pharmaceutical ingredients purchased from compounding pharmacies and three tablets: generic, similar and reference (materials were purchased from a drugstore at the city of Santo André, SP, Brazil). By DSC analysis we found that for samples of enalapril maleate from the compounding pharmacies had their T_{onset} around 150 °C and the enthalpy of fusion between 173-213 °C. The X-ray powder diffraction analysis was performed to examine crystallinity of the samples. The Rietveld refinement was performed using the software Topas Academic V4.1³ from XRPD data and we verified a good agreement between the calculated and observed XRPD patterns of the samples. The SEM images of enalapril maleate revealed rectangular-like crystals of irregular sizes. A study of photo-degradation of the active pharmaceutical ingredient was performed, since light is an essential part of the stability study, which may induce several reactions such as isomerization. However, the results obtained by means of DSC and XRPD did not displayed any evidence the samples were degraded.

Acknowledgment: CNPq, FAPESP, PPG-Nano and CEM.

[1] Kiang YH; Hug A; Stephens PW; Xu W, *Journal of Pharmaceutical Science*. 2003, 92, 1844-1853. [2] Dharmendra Singhal, William Curatolo, *Advanced Drug Delivered Reviews*. 2004, 56, 335-347. [3] Coelho A; *Topas Academic V4.1*, in Coelho Software, Brisbane, Austrália, 2007.

Keywords: enalapril maleate, polymorphism, X-ray powder diffraction, Rietveld refinement.

MS11_P152

Neutron Diffraction Study and Luminescence Properties of Eu³⁺-doped Y₃(Al,Ga)₅O₁₂, Y₃(Al,In)₅O₁₂ and Y₃(Ga,In)₅O₁₂

Ramūnas Skaudžius^a, Denis V. Sheptyakov^b, Artūras Katelnikovas^a, David Enseling^c, Thomas Jüstel^c, Christian Rüegg^{b,d} & Aivaras Kareiva^a

^aVilnius University, Lithuania

^bPaul Scherrer Institute, Switzerland

^cUniversity of Applied Science Muenster, Germany

^dUniversity of Geneva, Switzerland

e-mail: ramunas.skaudzius@chf.stud.vu.lt

Inorganic materials doped with Eu³⁺ are successfully employed as orange/red emitting phosphors. These compounds are important components in light-emitting diodes, fluorescence lamps, cathode ray tubes, field emission displays, electroluminescence displays and plasma display panels [1–4].

Yttrium aluminium and yttrium gallium garnets (Y₃Al₅O₁₂ (YAG) and Y₃Ga₅O₁₂ (YGG), respectively) are widely used as core host materials in luminescence [1, 5], while yttrium indium garnet (Y₃In₅O₁₂) is not obtained at the same conditions. The chemical composition and structure of the host materials influence the optical properties of such materials. Therefore, in the present work the matrices of YAG and YGG were modified by substituting aluminium with gallium or indium and gallium with indium. The modified matrices were doped with 1% Eu.

The sol–gel route has been successfully used to obtain europium doped Y₃(Al,Ga)₅O₁₂, Y₃(Al,In)₅O₁₂ and Y₃(Ga,In)₅O₁₂ powders. X-ray and neutron diffraction were used for phase identification and refinement of the crystal structures. The investigation has shown that all the samples follow the Vegard's law: the lattice parameter is increased linearly as a function of the concentration of the constituent elements. Moreover, these techniques helped to clarify the preferred positions of aluminium, gallium and indium ions in the tetrahedral and octahedral sites in the crystal lattice. The results are in good agreement with the work done by Nakatsuka *et al.* and Rodic *et al.* [6, 7].

The luminescence properties of the synthesized samples were characterized by VUV and UV/Vis spectroscopy, showing dominant emission of ⁵D₀ → ⁷F₄ transitions (680–720 nm wavelength range) under 160 nm wavelength excitation. The optical properties of Eu³⁺ in the different mixed-metal garnet matrices were explained in combination with the diffraction results. It

was demonstrated that more distorted 8 coordinated site more expressed the red emission of Eu^{3+} in the emission spectrum.

R.S. is thankful for the Sciex-NMSch and DAAD Fellowships to stay at Paul Scherrer Institute and Muenster University of Applied Sciences, respectively.

[1] T. Jüstel, H. Nikol, C. Ronda, *Angew Chem Int Edit*, 1998, 37, 3084-3103 [2] Q.Y. Zhang, X.Y. Huang, *Prog Mat Sci*, 2010, 55, 353-427 [3] J. Hou, X. Yin, Y. Fang, F. Huang, W. Jiang, *Opt Mater*, 2012, 34, 1394-1397 [4] C. Sommer, P. Hartmann, P. Pachler, H. Hoschopf, F.P. Wenzl, *J Alloy Compd*, 2012, 520, 146-152 [5] C. D. Brandle, R. L. Barns, *J Cryst Growth*, 1974, 26, 971-974 [6] A. Nakatsuka, A. Yoshiasa, T. Yamanaka, *Acta Cryst*, 1999, B55, 266-272 [7] D. Rodic, M. Mitric, R. Tellgren, H. Rundolof, *J Magn Magn Mater*, 2001, 232, 1-8

Keywords: Garnet, Refinement, Europium Emission

MS11_P153

Temperature stability studies of $\text{Yb}^{3+}/\text{Tm}^{3+}$ co-doped crystalline core-shell nanoparticles

Diana Thomas^a, Gökhan Dumlupinar^b, Haichun Liu^b, Maria E. Messing^b & Sefan Andersson-Engels^b

^aMAX IV Laboratory, Sweden; ^bLund University, Sweden
e-mail: diana.thomas@maxlab.lu.se

Frequency upconverting nanoparticles co-doped with rare- earth ions have shown great potential as contrast agents in biomedical imaging as well as laser applications due to their unique nonlinear optical properties [1,2]. Nanoparticles like $\text{NaYF}_4:\text{Yb}^{3+},\text{Tm}^{3+}/\text{NaYF}_4$ have their excitation wavelength and their main emission band in the so called “window of optical transparency” for biological tissues [3]. This property makes it possible to get images of deeply located bio-targets. The crystallographic structure and size of the core-shell particle have a significant influence on their required optical property.

In the presented study nanoparticles with different shell thickness were produced using a sequential preparation technique, where core and shell show a hexagonal structure. Since the shell is formed in a separate preparation step thermal stability (phase and size stability) of the core is of particular interest. For that reason both core only and core- shell particles were analysed by means of X-ray diffraction at beamline I711 at MAX IV Laboratory, respectively. The samples

(core only and core-shell particles in hexane solution) were heated up in air to 700 °C to investigate structural changes, such as phase transformations and changes in particle size *in situ*.

The phase transition from hexagonal to cubic structure occurred at temperatures above 500 °C for both core only and core-shell nanoparticles. The formation of oxide and fluoride structures started at even higher temperatures. This knowledge on the phase transition will help to improve the particle synthesis in future.

In addition, transmission electron microscopy (TEM) images and dynamic light scattering (DLS) were recorded on the as prepared samples. The particle sizes measured by TEM and DLS are comparable to the XRD line profile analyses results within the error.

[1] F. Auzel, *Chem. Rev.*, 2004, 104, 139–173, [2] D. K. Chatterjee, A. J. Rufaihah and Y. Zhang, *Biomaterials*, 2008, 29, 937–943, [3] M. Nyk, R. Kumar, T. Y. Ohulchanskyy, E. J. Bergey and P. N. Prasad, *Nano Letters*, 2008, 8, 3834–3838

Keywords: Core-shell nanoparticles, XRD line profile analyses, frequency upconversion

MS11_P154

Core polarization of silicon

Nanna Wahlberg^a, Niels Bindzus^a, Lasse Bjerg^a, Tine Straasø^b, J. Becker^a & B. B. Iversen^a

^aAarhus University, Denmark, nawa@chem.au.dk
^bUniversity of Copenhagen, Denmark

The electron density is often modeled by the Hansen-Coppens multipole model (HC model), where the valence density is modeled aspherically. Thus the HC model assumes an inert core density. Traditionally, the inert core has not been challenged, but the recent advantages in the field of powder crystallography allow us to model these very subtle core deformations. The core density can be modeled by extending the HC model to include similar refineable parameters as the valence density (the extended HC model, EHC). The EHC model have successfully been applied to diamond where both theoretical and experimental data of a sufficient quality was available.[1, 2]

Determining core polarization from experimental data requires high resolution and low extinction. Low extinction can be obtained by powder diffraction, while high resolution is obtained by using synchrotron

radiation. A special designed vacuum diffractometer further increases the signal-to-noise ratio by minimizing the air scattering. [3]

Compared to diamond, silicon is more complicated: The core density is known to be aspherically deformed. Further, the thermal displacement of the silicone atoms is more pronounced, which renders the measurement of high order reflection at room temperature. These reflections are crucial to obtain an electron density model containing the core deformations, since the high order reflections contain the information on the localized core density. The vacuum diffractometer have been equipped with a cooling devise, allowing measurements at 100K, which may reveal the nature of the static electron density in the inner silicon atom.

[1]: A. Fisher, D. Tiana, W. Scherer, K. Batke, G. Eickerling, H. Svendsen, N. Bindzus, and B. B. Iversen, *J. Phys. Chem.* 2011, 115, 13061 [2]: N. Bindzus, T. Straasø, N. Wahlberg, J. Becker, L. Bjerg, N. Lock, A.-C. Dippel, and B. B. Iversen, *Acta Crystallograp.* 2014, B70, 39 [3]: T. Straasø, J. Becker, B. B. Iversen and J. Als-Nielsen, *Synchrotron Rad.*, 2013, 20, 98

Keywords: Charge density, Core polarization, extended Hansen-Coppens model, High-resolution powder diffraction

*Microsymposium MS12:
Diffraction under pressure*

Chairs: Martin Bremholm, Aarhus University (DK)

Leonid Dubrovinsky, University of Bayreuth (DE)

Microsymposium: Wednesday 18 June 2014 Afternoon – iNANO building, 1593-012

Poster session: Monday 16 June 2014 – iNANO building, 1590-Foyer

Keynote Lecturers:

MS12_K1

Advanced synchrotron techniques to study materials in-situ at high pressure and temperature

[Vitali B. Prakapenka](#)

*Center for Advanced Radiation Sources, University of Chicago, Chicago, Illinois 60637, USA,
e-mail: prakapenka@cars.uchicago.edu*

High pressure research has made substantial progress in the last two decades in various fields of science mainly due to significant advances in the development of both high pressure vessels (diamond anvil cell and large volume press) and high-brilliant x-ray sources with unique synchrotron-based techniques optimized for high pressure studies, including high resolution x-ray micro-diffraction and total scattering, x-ray spectroscopy, micro-imaging, inelastic and nuclear resonance scattering. Combination of double-sided laser heating with synchrotron x-ray radiation has stimulated synthesis and investigation of new materials with unique composition and properties in-situ at high temperatures and high pressures in the diamond anvil cell [1]. Equation of state, structure, phase transformations, element partitioning, electronic and optical properties of various materials (single crystal, powder, nano-crystalline, amorphous solid and fluids) have been successfully studied at extreme conditions with help of lasers and x-ray beams.

Recent developments in pulse laser heating technique, including application of fiber lasers and flat top laser beam shaping optics, result in significant improvement in synthesis of new metastable materials with tunable composition and properties controlled in-situ with high resolution x-ray and optical techniques in the time-domain mode. However, using the diamond anvil cell to generate high pressure we substantially sacrificing x-ray diffraction data quality due to number of constraints: very small sample size, relatively high background (Compton scattering from diamond anvils), limited x-ray opening etc. Various experimental approaches should be employed for reliable sample characterization. The details of diamond anvil cell experimental methods and recent advances in the synchrotron x-ray diffraction technique for studies unique physical and chemical properties of materials in-situ at extreme conditions up to 600 GPa and 6000 K will be discussed.

[1] V. B. Prakapenka et al, *High Pressure Research*. 2008, **28** (3), 225-235

Keywords: x-ray diffraction, high pressure, high temperature, laser heating, time domain

MS12_K2

Neutron Diffraction at High Pressure at IBR-2 Reactor: Current State and Prospects

[Sergey Kichanov](#), Denis Kozlenko, Evgeniy Lukin & Boris Savenko

Frank Laboratory of Neutron Physics, Joint Institute for Nuclear Research, 141980 Dubna, Russia

The dramatic progress in extreme condition research is caused by a discovery of great number of novel interesting phenomena in condensed matter physics and material science, chemistry, geophysics and planetary research. In a comparison to other experimental methods, the application of high pressure is a direct method of controlled changing of some physical properties by means of variation of interatomic distances and angles. However, the evolution of high-pressure neutron diffraction methods is seriously restricted by drastically low intensity of neutron sources (in many orders of magnitude) in comparison with synchrotron radiation one. Nonetheless, the neutron diffraction has many advantages for studies of the crystal structure of materials containing light atoms like hydrogen and oxygen and, especially, for studies of the magnetic structure of materials. This provokes motivation of development in neutron scattering techniques over a sufficiently wide range of pressures (0–10 GPa and higher).

My talk is focused on recent progress in neutron diffraction techniques and methods for research under extreme conditions at IBR-2 high flux pulsed reactor. The recent results of studies of complex manganese and iron oxides at high pressures up to 13 GPa using sapphire anvil high pressure cells are presented. The prospects for further progress in development of neutron scattering techniques at IBR-2 reactor under extreme conditions are discussed.

Keywords: neutron diffraction, high pressure

Oral Presentations:

MS12_O1

Critical behaviour in molecular frameworks: understanding the origin of negative thermal expansion in zinc (II) cyanide

[Andrew B. Cairns](#)^a, [Ines E. Collings](#)^a, [Amber L. Thompson](#)^a, [Julia E. Parker](#)^b, [Chiu C. Tang](#)^b, [Matthew G. Tucker](#)^{b,c}, [Jadna Catafesta](#)^d, [Claire Levelut](#)^d, [Julien Haines](#)^d, [Vladimir Dmitriev](#)^e, [Philip Pattison](#)^f & [Andrew L. Goodwin](#)^a

^aDepartment of Chemistry, University of Oxford, Inorganic Chemistry Laboratory, South Parks Road, Oxford, OX1 3QR, U.K.

^bDiamond Light Source, Chilton, Oxfordshire, OX11 0DE, U.K.

^cISIS Facility, Harwell Science and Innovation Campus, Didcot, OX11 0QX, U.K.

^dUniversité Montpellier 2, 34095, Montpellier, France

^eSwiss-Norwegian Beamlines, ESRF, Polygone Scientifique Louis Néel, 38000, Grenoble, France

^fCrystallography Competence Centre, École Polytechnique Fédérale de Lausanne, BSP, CH-1015 Lausanne, Switzerland
e-mail: andrew.cairns@chem.ox.ac.uk

Molecular frameworks—materials constructed from metal nodes connected by a molecular linker—have received much attention due to their very flexible structures that give rise to a host of unusual mechanical properties [1]. Perhaps the most studied of these is the negative thermal expansion (NTE) response, where the material shrinks in one or more directions on heating, which is found in many cyanide and metal–organic frameworks [2]. The fundamental consequence of using molecular rather than single-atom bridges to assemble frameworks is the dominance of low-energy dynamics, and therefore the magnitude of these unusual responses are often much larger than in traditional materials [3]. Despite a huge amount of interest in these materials and their unusual responses, the microscopic mechanisms are not well understood.

We have studied the mechanism of NTE in the relatively simple but canonical isotropic NTE material $\text{Zn}(\text{CN})_2$ [2] by considering the critical behaviour of the system under pressure [4]. By analysing variable-pressure powder diffraction data, we identified the intrinsic phase transition at 1.52 GPa and were able to solve the previously unknown high-pressure structure. As the same low-energy phonon modes are implicated in both phase transition and unusual thermomechanical responses, we were able to relate the static distortions observed in the high-pressure phase to the dynamics of the ambient pressure phase. For the first time we have been able to observe directly the mechanism of NTE in $\text{Zn}(\text{CN})_2$, and furthermore rationalise other unusual phenomena in the system such as the softening of the structure under pressure and negative linear

compressibility (NLC) in the high-pressure structure. This study reveals parallels to both related systems, such as $\text{Cd}(\text{CN})_2$, and links to much more exotic physics in flexible systems.

[1] C. J. Kepert, *Chem. Commun.* 2006, 695–700 [2] A. L. Goodwin & C. J. Kepert, *Phys. Rev. B* 2005, 71, 140301(R) [3] A. B. Cairns & A. L. Goodwin, *Chem. Soc. Rev.* 2013, 42, 4881–4893 [4] I. E. Collings *et al.*, *J. Am. Chem. Soc.* 2013, 135, 7610–7620

Keywords: critical phenomena, thermal expansion, coordination polymers

MS12_O2

Dramatic softening of the negative thermal expansion material HfW_2O_8 on heating through its WO_4 orientational order-disorder phase transition

[Leighanne Gallington](#)^a & [Angus P. Wilkinson](#)^a

^aGeorgia Institute of Technology, USA
e-mail: lgallington3@gatech.edu

Cubic ZrW_2O_8 , which exhibits isotropic negative thermal expansion, has been previously examined as a potential component in a variety of controlled thermal expansion composites. However, this material and its close relative HfW_2O_8 undergo a phase transition ($\alpha \rightarrow \beta$) associated with orientational disordering of WO_4 pairs upon heating that results in a reduction in the magnitude of its coefficient of thermal expansion (CTE).

The effect of hydrostatic pressure on the CTEs of cubic HfW_2O_8 was investigated using high energy synchrotron x-ray powder diffraction along with a recently designed cell suitable for the precise control of temperature and hydrostatic pressure. This novel cell design uses internal collimation to largely eliminate parasitic scattering from the titanium pressure vessel [1].

In a previous study in this environment, ZrW_2O_8 underwent a phase transition to the well-known marginally NTE orthorhombic phase between 343K and 357K at pressures above 210 MPa [2]. No such transition was observed for HfW_2O_8 at pressures up to 411 MPa, allowing for exclusive focus on the cubic phase.

In cubic HfW_2O_8 , for temperatures just below its α - β phase transition, the application of pressure induced

reversible orientational disordering of WO_4 pairs between 416K and 459K. A 31% reduction in bulk modulus (69.7 GPa to 48.0 GPa) between 298 and 430K at pressures between 52 and 411 MPa was observed. Additionally, pressure-induced softening was observed: at 416 K, the bulk modulus between 259 and 411 MPa was 29% lower than that between 52 and 207 MPa. The CTE of $\alpha\text{-HfW}_2\text{O}_8$ (298-430K) increased in magnitude from -10 ppm/K at 52 MPa to -15 ppm/K at 411 MPa. In contrast, $\beta\text{-HfW}_2\text{O}_8$ stiffened slightly upon heating and the magnitude of the CTE was only marginally reduced upon compression. These results suggest that the effects of stress and temperature should be considered carefully when designing controlled thermal expansion composites incorporating HfW_2O_8 .

[1] Wilkinson AP, Morelock CR, Greve BK, Jupe AC, Chapman KW, Chupas PJ, Kurtz C. *J. Appl. Crystallogr.* 2011, 44(5), 1047 [2] Gallington LC, Chapman KW, Morelock CR, Chupas PJ Wilkinson AP, *PCCP*. 2013, 15(45), 19665

Keywords: pressure-induced softening, negative thermal expansion, order-disorder phase transitions, *in situ* high pressure x-ray diffraction

MS12_O3

K_2CO_3 at high pressures: powder diffraction experiment and structure prediction

Pavel Gavryushkin^{a,b}, Anna Likhacheva^a, Zakhar Popov^c, Anton Shatskiy^{a,b}, Konstatin Litasov^{a,b}, Sergey V. Rashchenko^{a,b}, Yuji Higo^d & Ken-ichi Funakoshi^d

^aV.S. Sobolev Institute of Geology and Mineralogy, Russian Academy of Science, Siberian Branch, Russia

^bNovosibirsk State University, Russia

^cKirensky Institute of Physics, Russian Academy of Science, Siberian Branch, Russia

^dSPRING-8, Japan Synchrotron Radiation Research Institute, Japan
e-mail: p.gavryushkin@gmail.com

Structural transformations of K_2CO_3 have been studied in details at high temperatures, but for high pressures there is no experimental and only one theoretical work [1], according to which at 8.4–27.5 kbar $\gamma\text{-K}_2\text{CO}_3$ adopt $\gamma\text{-Na}_2\text{CO}_3$ structure.

Two series of synchrotron powder diffraction experiments were carried out.

First series of experiment: energy dispersive, SPring-8 (Japan), Kawai-type multi-anvil apparatuses [2,3], pressure-temperature range 1–105 kbar, 298-1273 K. Ambient $\gamma\text{-K}_2\text{CO}_3$ is transformed in the new phase denoted as $\text{K}_2\text{CO}_3\text{-II}$ between 1 and 33 kbar at 298 K.

$\text{K}_2\text{CO}_3\text{-II}$ is stable at all investigated pressure-temperatures range.

Second series of experiment: angle dispersive, SSRC Synchrotron Centre (Russia) [4], pressures 4.5–31 kbar, temperature 298K. The pressure of phase transition $\gamma\text{-K}_2\text{CO}_3 \rightarrow \text{K}_2\text{CO}_3\text{-II}$ was ascertained to 23.5–28 kbar. Diffraction pattern of $\text{K}_2\text{CO}_3\text{-II}$ at 31 kbar was indexed with McMaile software [5]:

$a=8.6149(6)\text{\AA}$, $b=5.9106(5)\text{\AA}$, $c=6.98599(36)\text{\AA}$,
 $\beta=103.68^\circ(6)$ \AA .

The comparison of theoretically predicted structure [1] with experimental diffraction patterns shows that theoretical structure doesn't confirm to $\text{K}_2\text{CO}_3\text{-II}$. We carried out structure prediction of K_2CO_3 for $Z=4$ with USPEX code [6-10], based on ab-initio total-energy program VASP [11,12] and found out new metastable phase denoted as $\text{K}_2\text{CO}_3\text{-II}'$:

$a=8.89312\text{\AA}$, $b=5.95732\text{\AA}$, $c=6.92902\text{\AA}$, $\beta=104.17^\circ$, $P2_1/c$.

Based on the good agreement of structural data on this phase with powder diffraction pattern it can be concluded that theoretical $\text{K}_2\text{CO}_3\text{-II}'$ correspond to experimental $\text{K}_2\text{CO}_3\text{-II}$. Of course, final decision can be made only after refinement against powder diffraction pattern. In the case of successful refinement, it will be the interesting example of using structure prediction methods for crystal structure solution from powder diffraction data.

The research was supported by the Russian Foundation for Basic Research, project № 14-05-31051 and Ministry of Education and Science of Russia, project № 14B25.31.0032.

[1] Cancarevic, Z., J. C. Schon, and M. Jansen, *Z. Anorg. Allg. Chem.* 2006, 632(8-9), 1437-1448. [2] Katsura, T., K. Funakoshi, A. Kubo, N. Nishiyama, Y. Tange, Y. Sueda, T. Kubo, and W. Utsumi, *PEPI*. 2004, 143, 497-506. [3] Litasov, K., E. Ohtani, A. Sano, A. Suzuki, and K. Funakoshi, *E.* 2005, 238(3-4), 311-328. [4] Ancharov, A. I., A. Y. Manakov, N. A. Mezentssev, B. P. Tolochko, M. A. Sheromov, and V. M. Tsukanov, *Nuclear Instruments & Methods in Physics Research A*. 2001, 470(1-2), 80-83. [5] Le Bail, A., *Powder Diffraction*. 2004, 19(3), 249-254. [6] Oganov, A. R., C. W. Glass, and S. Ono (2006), *Earth Planet. Sci. Lett.* 241(1-2), 95-103. [7] Oganov, A. R., and C. W. Glass (2006), *J. Chem. Phys.*, 124(24). [8] Lyakhov, A. O., A. R. Oganov, and M. Valle (2010), *Comput. Phys. Commun.*, 181(9), 1623-1632. [9] Lyakhov, A. O., A. R. Oganov, H. T. Stokes, and Q. Zhu (2013), *Comput. Phys. Commun.*, 184(4), 1172-1182. [10] Glass, C. W., A. R. Oganov, and N. Hansen (2006), *Comput. Phys. Commun.* 175(11-12), 713-720. [11] Kresse, G., and J. Furthmuller (1996), *Comput. Mater. Sci.*, 6(1), 15-50. [12] Kresse, G., and D. Joubert (1999), *Phys Rev B*, 59(3), 1758-1775.

Keywords: potassium carbonate, alkali, high pressure, experiment, powder diffraction, phase transition, structure prediction, DFT, USPEX, VASP.

Microstructure defects in graphitic boron nitride: Analysis, modification and impact on the transition to sp³-hybridized BN

Christian Schimpf^a, Marcus Schwarz^b, Helge Schumann^a,
Christian Lathe^c, Edwin Kroke^b & David Rafaja^a

^aTU Bergakademie Freiberg, Institute of Materials Science, Germany, e-mail: schimpf@iwwww.tu-freiberg.de

^bTU Bergakademie Freiberg, Institute of Inorganic Chemistry, Germany,
^cGeoForschungszentrum Potsdam, Germany,

The high pressure/high temperature (HP/HT) conversion of hexagonal, graphitic boron nitride (h-BN) in its high density modifications, i.e., wurtzitic (w) and cubic (c) BN, is controlled by the synthesis parameters as well as by the microstructure of the h-BN precursor. The effect of the microstructure on the phase transition can be characterized thoroughly by applying X-ray powder diffraction (XRD). The h-BN is known to contain a large variety of microstructure defects [1] like stacking faults, dislocations, turbostratic disorder and corrugated basal planes. In this contribution, we will illustrate some examples, how the dominating defect types in this material can be recognized and analyzed (semi)quantitatively on the basis of the dependence of the X-ray diffraction line broadening on the crystallographic direction [2]. The results obtained with XRD are verified by transmission electron microscopy with high resolution.

Furthermore, it will be discussed how the kind and density of the microstructure defects in the h-BN precursor can be altered by thermal treatment. It turned out that i.e. the turbostratic disorder and the basal plane corrugations require significantly different conditions for their recovery. Thus, annealing is a viable tool to control the microstructure of the h-BN precursor, which in turn offers a possibility to manufacture HP/HT composite materials with desired properties. The significance of this research is given by the fact that boron nanocomposites containing a crystallographically interlocked mixture of all three BN phases show superior properties over their phase-pure or even single-crystalline counterparts [3].

Finally, in-situ energy-dispersive XRD under high pressure was applied to study the transformation behavior of h-BN into its wurtzitic (w-BN) and cubic modification (c-BN) as a function of the microstructure of the h-BN precursor. The role that the microstructure defects play during this phase transition will be discussed.

[1] J.Y. Huang, Y.T. Zhu, *Defect Diffus. Forum.* 2000, 186-187, 1-32

[2] C. Schimpf, M. Motylenko, D. Rafaja, *Mater. Char.* 2013, 86, 190

[3] D. Rafaja, et. al. , *Chem. Soc. Rev.* 2012, 41, 5081-5101

Keywords: boron nitride, microstructure defects, X-ray diffraction, high pressure/high temperature

Posters:

MS12_P155

Advances in High Pressure Diffraction Techniques at the ISIS Neutron Facility

[Craig L Bull](#), [William G Marshall](#) & [Matthew G Tucker](#)

ISIS Facility, Rutherford Appleton Laboratory, Harwell Campus, Didcot, Oxon, OX11 0QX, UK

The Pearl High Pressure Facility is a medium resolution high-flux neutron powder diffractometer optimised for data collection from the Paris-Edinburgh pressure cell. The instrument is situated on target station one of the ISIS Neutron Spallation Facility in the UK.

Taking examples from experiments performed on the Pearl instrument, we will present recent scientific highlights from high pressure powder studies of a wide range of materials including studies performed on novel elpasolite perovskites, hydrogen bonded materials and geologically relevant materials, where the advantages of neutron powder diffraction have been clearly used. These experiments have made use of new anvil materials, low and high temperature setups and new instrument capabilities itself. We will also show developments which are currently in progress. Future envisaged high pressure developments will also be presented.

Keywords: High pressure, Neutron diffraction, large volume

MS12_P156

Structural behavior of hard and superhard materials under pressure

[Natalia Dubrovinskaia](#)^a, [Elena Bykova](#)^{a,b} & [Leonid Dubrovinsky](#)^b

^a*University of Bayreuth, Laboratory of Crystallography, Germany, e-mail: Natalia.Dubrovinskaia@uni-bayreuth.de*

^b*University of Bayreuth, Bayerisches Geoinstitut, Germany*

The development of new materials is an ultimate goal of modern science and technology. Contemporary advanced materials, with the quest for multifunctionality, are commonly tailor-made precisely because they exhibit a particular compromise or combination of characteristics that no simple materials

supply. Such an approach to materials development requires deep understanding of materials properties and their response to external effects. *In situ* investigations of the phenomena induced or tuned by external pressure are of great interest and importance for both fundamental and applied sciences

Observing structural and bond length changes, as well as measuring elastic properties of poorly compressible materials (carbides and borides) require very high pressures and high precision measurements which are difficult without synchrotron radiation. It is double true for light elements like boron and diamond-like materials. We apply combined powder and single crystal X-ray diffraction techniques using *in house* and synchrotron radiation facilities to characterize materials behavior at extreme conditions. Examples of investigations of novel carbon forms (nanocrystalline diamonds and aggregated diamond nanorods), boron and transition metal borides will be presented. In particular structural aspects of the anisotropy in elastic behavior of MnB₄, FeB₄, Fe₂B₇, and Fe_{1.04}B₅₀ will be discussed.

Keywords: hard materials, compressibility, high-pressure behavior

MS12_P157

Equations of state of metals from X-ray diffraction data at static pressures above 5 Mbar

[Leonid Dubrovinsky](#)^a & [Natalia Dubrovinskaia](#)^b

^a*University of Bayreuth, Bayerisches Geoinstitut, Germany
e-mail: Leonid.Dubrovinsky@uni-bayreuth.de*

^b*University of Bayreuth, Laboratory of Crystallography, Germany*

The impact of high-pressure studies on fundamental physics and chemistry, and especially on the Earth and planetary sciences, has been enormous. While experiments in diamond anvil cells (DACs) at pressures of ~250 - 400 GPa are proven to be very difficult but possible, at higher static pressures any matter has not been investigated until very recently. We have developed a method of synthesis of balls and semi-balls (of 10 to 50 μm in diameter) made of nanodiamond (with individual nano-particles of linear dimensions below 30 nm) and used them as second-stage or indenter-type anvils in conventional DACs. In experiments on rhenium, osmium, gold, platinum, and tungsten we were able to generate pressures above 700 GPa and demonstrated crucial necessity of the ultra-high pressure measurements for accurate determination

of the equation of state of materials at extreme conditions.

Keywords: equation of state, compressibility, high-pressure behavior

MS12_P158

In situ High-Pressure Powder Diffraction Study of Gadolinium and Holmium Orthovanadates

Olga Ermakova^{a,b}, Roman Minikayev^a, Stefan Carlson^c, Agata Kaminska^a, Stanislaw Gierlotka^d, Francisco Martinez^c, Michal Glowacki^a, Marcin Czech^a, Marek Berkowski^a & Wojciech Paszkowicz^a

^aInstitute of Physics of Polish Academy of Sciences, Poland

^bSolid State Chemistry Institute of Russian Academy of Sciences, Russian Federation

^cMAXlab, Sweden

^dInstitute of High Pressure Physics of Polish Academy of Sciences, Poland
e-mail: Olga.N.Ermakova@gmail.com

Rare-earth orthovanadates (RVO₄) are materials which may have wide applications as laser materials, catalysts, waveguides etc. [1, 2, 3] They are characterized by pressure initiated zircon-scheelite (or monazite) phase transition in the pressure range of 5-10 GPa.

In present study, structure parameters of scheelite-type phase of gadolinium and holmium orthovanadates (GdVO₄ and HoVO₄) and elastic properties for both zircon- and scheelite-type polymorphs of above mentioned materials were determined by fitting of Birch-Murnaghan equation of state.

For determination of elastic properties, in situ high-pressure powder diffraction experiments were carried out at I711 beamline of MAX IV synchrotron in Maxlab (Lund, Sweden) using a diamond anvil cell. Experiments were performed in hydrostatic conditions (methanol-ethanol-water mixture as pressure transmitting medium) at pressure range up to 10 GPa. Obtained powder diffraction data were treated by Rietveld method and obtained V(p) curves were used for determination of equation-of-state parameters with EosFit52 software. Structure parameters for scheelite-type phase of GdVO₄ and HoVO₄ were calculated employing the Rietveld method for laboratory powder diffraction data. The initially prepared samples had the zircon-type structure. The GdVO₄ sample was prepared as a product of solid state reaction between Gd₂O₃ and V₂O₅ oxides. The HoVO₄ sample was grown in the single crystal form by Czochralski method. For

preparation of scheelite-type structure, these samples were pressed up to 7 GPa with simultaneous heating up to 650° C during 15 min.

Determined structure parameters and bulk moduli for studied GdVO₄ and HoVO₄ samples show good resemblance to those of other members of RVO₄ family. During the in situ study, the zircon-scheelite phase transition was achieved for both materials.

[1] R.A. Fields, M. Birnbaum, C.L. Fincher, *Appl. Phys. Lett.* 1987, 51, 1885

[2] A.I. Zagumennyi, V.G. Ostroumov, I.A. Shcherbakov, T. Jensen, J.P. Meyen, G. Huber, *Sov. J. Quantum Electron.* 1992, 22, 1071

[3] F. Chen, X. Wang, S. Li, G. Fu, K. Wang, Q. Lu, D. Shen, R. Nie, H. Ma, *J. of Appl. Phys.*, 2003, 94.7, 4708-4710.

Keywords: rare-earth, orthovanadates, in situ, high pressure

MS12_P159

Combining high-pressure powder x-ray diffraction and Mössbauer spectroscopy

Eran Greenberg^a, Gregory Rozenberg^a, Weiming Xu^a, Moshe Paz Pasternak^a, Leonid Dubrovinsky^b, Vitali Prakapenka^c & Zuzana Konopkova^d

^aTel-Aviv University, Israel

^bBayerisches Geoinstitut, Germany

^cUniversity of Chicago CARS, USA

^dDESY Photon Science, Germany

The study of structural phase transitions at high pressures using powder x-ray diffraction is often limited due to the inability of measuring individual intensities. Therefore the accuracy of the high pressure diffraction study is not sufficient for unambiguous interpretation of the obtained structural results. In such a case Mössbauer spectroscopy (MS), as an atomic-scale structural and magnetic/electronic probe, can provide missing information necessary for constructing a structural model. Thus, in Fe-based compounds MS can provide additional structural information such as the number of different crystallographic sites occupied by the Fe cations, their relative multiplicities and other characteristics.

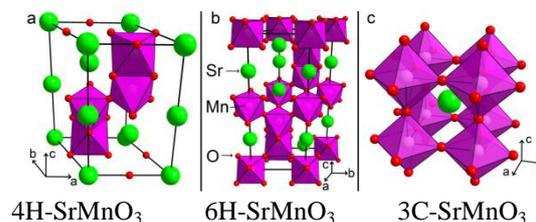
In this talk we present a few examples of such a fruitful interaction of methods demonstrating how high-pressure MS provided information for determining the nature of the transitions including cases in which the structural transition is related to an electronic/magnetic transition. Fe₂O₃ hematite, Fe₃O₄ magnetite [1], Fe₂SiO₄

ringwoodite [2], GaFeO_3 [3] and CaFe_2O_4 [4] are given as example cases for the impact of Mössbauer Spectroscopy on High Pressure Crystallography studies.

- [1] Rozenberg, Pasternak, Xu, Amiel, Hanfland, Amboage, Taylor, Jeanloz, *Phys. Rev. Lett.*, 2006, 96, 045705
 [2] Greenberg, Dubrovinsky, McCammon, Rouquette, Kantor, Prakapenka, Rozenberg, Pasternak, *American Mineralogist*, 2011, 96, 833-840
 [3] Arielly, Xu, Greenberg, Rozenberg, Pasternak, Garbarino, Clark, Jeanloz, *Phys. Rev. B.*, 2011, 84, 094109
 [4] Greenberg, Rozenberg, Xu, Pasternak, McCammon, Glazyrin, Dubrovinsky, *Phys. Rev. B.*, 2013, 88, 214109.

Keywords: high-pressure, powder diffraction, Mössbauer Spectroscopy

first steps towards a full P - T phase diagram for SrMnO_3 .



Keywords: Perovskite, high pressure, high temperature, polymorphism, solid state reactions

MS12_P160

Phase stability of the SrMnO_3 hexagonal perovskite system at high pressure and temperature

Morten Schulz Bormann Nielsen^a, Davide Ceresoli^b, Paraskevas Parisiades^c, Vitali B. Prakapenka^d, Tony Yu^d, Yanbin Wang^d & Martin Bremholm^a

^a Center for Materials Crystallography, Langelandsgade 140, Aarhus University, Denmark, Email: mortensn@inano.au.dk

^b Center for Materials Crystallography and Institute of Molecular Science and Technology (CNR-ISTM), Milano University, Italy

^c European Synchrotron Radiation Facility, Beamline ID27, France
^d Center for Advanced Radiation Sources, University of Chicago, USA

In the SrMnO_3 hexagonal perovskite system, three polymorphs can be stabilized to ambient conditions: Two hexagonal phases, 4H and 6H (seen below as a and b), and the classic 3C perovskite structure (seen as c below). This many polymorphs at ambient conditions is a rare sight for perovskites, making the compound a good choice for a case study of the energetic interplay between the possible polymorphs.

In this study, we measured the first experimental equations of state of the 6H and 3C polymorphs and also conducted the first in situ observations of transformations between all three known polymorphs, under high pressure and high temperature conditions.

Our own DFT calculations were combined with the experimental results to gain insight into the energetic relations between the phases. By combining our findings with literature, we have been able to take the

MS12_P161

Exploring the mechanical properties of flexible MOFs by coupling experimental and modelling approaches

Pascal G. Yot^a, Paul Fabry^b, Fabrice Salles^a, Patricia Horcajada^b, Thomas Devic^b, Christian Serre^b & Guillaume Maurin^a

^a University of Montpellier, France, e-mail: pascal.yot@um2.fr, fabric.salles@um2.fr, guillaume.maurin@um2.fr

^b University of Versailles, France, e-mail: horcajada@uvsq.fr, devic@uvsq.fr, serre@uvsq.fr

The stability of the Metal Organic Frameworks towards temperature, humidity and applied mechanical pressure are of great interest for further industrial applications in the field of adsorption and catalysis [1]. The mechanical behaviour of such porous solids became topical only a few years ago, however only a restricted class of MOF materials has been investigated so far: (i) the zeolitic imidazolate framework (ZIFs) and IRMOFs solids [2] and (ii) more recently, the isostructural MIL-53(Cr) and MIL-47(V) (MIL for Material of Institut Lavoisier) materials [3-4]. In parallel, the influence of different confined fluids, mainly alcohols, on the pressure induced amorphization of a few MOFs including HKUST-1, MOF-5 and ZIF-8 has been also explored in a very high pressure domain (>1GPa) [5-7].

Following our previous findings on the behavior of flexible MOFs upon moderate applied pressure [3-4], here we have investigated the mechanical properties of the breathing MIL-53(M^{III}) family (with M=Al, Cr, Fe...) and its functionalized form MIL-53(Cr)_X (with X=Cl, CH₃,...) under high mechanical pressure up to 2 GPa. These MOFs materials have been characterized starting with their hydrated states and using different

conditions with non- and penetrating fluid and advanced experimental techniques including X-ray and Neutron powder diffractions, Raman spectroscopy and Hg-porosimetry, coupled with Molecular Dynamics simulations based newly developed forcefields. We have evidenced that (i) the nature of the grafted ligands, (ii) the hydration degree, and (iii) the type isostatic fluid used (polar or apolar) significantly influence the mechanical behavior of this class of solids. For each explored couple of compound-condition, the equation of state and bulk modulus have been established in a wide range of pressure.

[1] Metal-organic frameworks, *Chem. Soc. Rev.* 2009 **38** 1201; *Chem. Rev.* 2012 **112** 673 [2] J.C. Tan *et al.*, *Chem. Soc. Rev.* 2011 **40** 1059 [3] P.G. Yot *et al.*, *Chem. Sci.* 2012 **3** 1100 [4] Q. Ma *et al.*, *Dalton Trans.* 2012 **41** 3915 [5] K. W. Chapman *et al.*, *J. Am. Chem. Soc.* 2008 **130** 10524 [6] A. J. Graham *et al.*, *Angew. Chem. Int. Ed.* 2011 **50** 11138 [7] S. A. Moggach *et al.*, *Angew. Chem. Int. Ed.* 2009 **48** 7087

Keywords: Powder diffraction under pressure, Pressure induced phase changes, Metal-Organic Framework Materials, Molecular simulations

MS12_P162

Ir—Os alloys under high-pressure

Kirill V. Yusenko^a, Elena A. Bykova^b, Serena Margadonna^a & Leonid S. Dubrovinsky^b

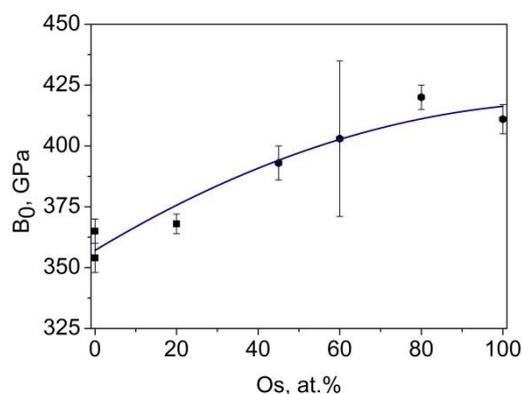
^aUniversity of Oslo, Norway, e-mail: kirill.yusenko@smn.uio.no
^bBayerisches Geoinstitut, Universität Bayreuth, Germany

Heavy transition metals especially platinum group metals (PGM) show high densities and extremely high melting points, as well as mechanical, thermal and chemical stabilities. Their low compressibility under high-pressure reveal the perspectives for their application under extreme conditions. Investigations of PGM alloys under extreme conditions may allow understand mechanical properties, phase stability and electronic structure of such materials. Pure PGM show no temperature and pressure induced transformations as well as their solid solutions show no tendency for formation ordered phases under ambient pressure.

Observation of *fcc*↔*hcp* pressure and temperature induced phase transformations unknown for pure metals may improve our knowledge about thermodynamic and structural properties of compositions relevant for understanding a formation of PGM minerals such as iridosmine and related phases.

Here we report our study of compressibility for *fcc* and *hcp* Ir—Os solid solutions under high-pressure (up to 145 GPa) high-temperature (up to 3000°C) conditions in laser heated diamond-anvil cells. Binary single-phase Ir—Os alloys were prepared in a powder form from $(\text{NH}_4)_2[\text{Ir}_x\text{Os}_{1-x}\text{Cl}_6]$ by thermal decomposition at 600°C in hydrogen atmosphere. Compressibility curves were fitted using the third order Birch-Murnaghan equation of state with pressure derivative fixed as 4. The corresponding bulk moduli (B_0) are higher in comparison with pure Ir (354(6) GPa) and maximal value is characteristic for *hcp*-Ir_{0.20}Os_{0.80} which is slightly higher than B_0 for pure Os (411(6) GPa) and still smaller the diamond value (446(1) GPa, $B' = 3.0(1)$). Concentration dependence of bulk moduli for Ir—Os solid solutions shows a positive deviation from linearity (see figure below).

High-temperature data shows a dependence of miscibility gap on the pressure for the equilibrium binary Ir—Os phase diagram, which results in its shift to Ir (*fcc* solid solutions) part with pressure increase and direct observation of *hcp*→*fcc* P—T-induced transformation in *hcp*-Ir_{0.50}Os_{0.50} and T-induced phase separation (formation of *hcp*+*fcc* mixture).



[1] I.V. Korolkov, S.A. Gromilov, K.V. Yusenko, *et al.*, *J. Structur. Chem.* 2005, 46, 1052 [2] K.V. Yusenko, E.A. Bykova, S.A. Gromilov, *et al.*, *Phys. Rev. B* 2014, *submitted*

Keywords: iridium, osmium, high-pressure

Authors Index

A

Abdala P. [83](#)
 Abdellatif M. [86](#)
 Abdessalem B. [152](#), [153](#), [165](#),
[166](#)
 Abeykoon A. [28](#)
 Adam C. [135](#)
 Adamczyk B. [135](#)
 Adamson P. [81](#)
 Adel R. [152](#)
 Aizarna M. [127](#)
 Allan P. [66](#)
 Álvarez-Pinazo G. [112](#)
 Amara A. [123](#), [164](#)
 Amine D. [153](#)
 Ammar M. [123](#)
 Amri M. [108](#)
 Ancharova U. [21](#), [153](#)
 Andersen C. [154](#)
 Andersen H. [106](#), [109](#)
 Andersson-Engels S. [170](#)
 Andrieu F. [127](#)
 Aranda M. [112](#), [117](#), [156](#)
 Artioli G. [112](#)
 Ashahi T. [158](#)

B

Baerlocher C. [35](#), [168](#)
 Balmes O. [84](#)
 Ban V. [67](#)
 Barreiro E. [39](#)
 Barroso R. [39](#)
 Bart F. [18](#)
 Bassanetti I. [159](#)
 Bastida J. [94](#), [96](#)
 Batlogg B. [141](#)
 Bazaga-García M. [156](#)
 Becker J. [131](#), [155](#), [171](#)
 Beckers D. [85](#)
 Beerlink A. [83](#)
 Behrooz A. [154](#)
 Belin S. [121](#)
 Belaouad S. [58](#)
 Benmokhtar S. [58](#)
 Beran P. [155](#)
 Beranek L. [160](#)
 Berkowski M. [180](#)
 Bernasconi A. [17](#), [21](#)
 Bertelsen M. [82](#)
 Bertolotti F. [22](#), [36](#)
 Besenbacher F. [70](#)
 Beyerlein K. [150](#)

Bianchini M. [79](#)
 Biasi L. [109](#), [115](#)
 Billinge S. [28](#), [47](#), [106](#), [149](#)
 Binder J. [109](#), [115](#)
 Bindzus N. [23](#), [155](#), [171](#)
 Birgisson S. [17](#), [110](#)
 Birkbak M. [55](#)
 Birkedal H. [55](#), [70](#), [96](#), [116](#), [120](#)
 Bjerg L. [171](#)
 Blichfeld A. [131](#), [154](#), [158](#)
 Boldyreva E. [48](#)
 Bondesgaard M. [131](#)
 Bonemer de Salvi S. [49](#)
 Bordet P. [84](#), [150](#), [159](#)
 Borkiewicz O. [66](#), [67](#), [119](#), [122](#)
 Bot A. [152](#)
 Bowron D. [17](#)
 Boysen H. [87](#)
 Bozin E. [149](#)
 Braz D. [39](#)
 Bremholm M. [154](#), [181](#)
 Brink B. [111](#)
 Brito H. [161](#)
 Britto S. [67](#)
 Brooks L. [48](#)
 Broseghini M. [95](#)
 Brown C. [67](#)
 Brunátová T. [56](#), [99](#), [131](#)
 Brunelli M. [23](#), [48](#)
 Buckley C. [63](#), [64](#), [69](#)
 Bull C. [179](#)
 Bushinsky M. [143](#)
 Bushmarinov I. [38](#), [133](#)
 Bykova E. [179](#), [182](#)
 Bähz C. [167](#)
 Bøjesen E. [29](#), [72](#), [74](#), [106](#),
[109](#), [110](#), [115](#)

C

Cabeza A. [156](#)
 Cairns A. [19](#), [151](#), [176](#)
 Caldes M. [121](#)
 Capek J. [100](#)
 Carbone G. [127](#)
 Carlson S. [180](#)
 Carpenter M. [167](#)
 Carvalho J. [161](#)
 Castets G. [84](#)
 Catafesta J. [176](#)
 Cavalleri A. [150](#)
 Ceresoli D. [181](#)
 Ceretti M. [13](#)
 Cernik R. [53](#)

Černý R. [58](#), [65](#), [71](#)
 Cersoy S. [84](#)
 Cervellino A. [22](#), [36](#), [46](#), [130](#),
[143](#)
 Chalmin É. [84](#)
 Chaminade J. [37](#), [41](#)
 Chapman H. [150](#)
 Chapman K. [66](#), [67](#), [119](#), [122](#)
 Charaf A. [58](#)
 Chater P. [22](#)
 Chatterji T. [167](#)
 Checchia S. [23](#)
 Chen H. [54](#)
 Cherepanova S. [21](#)
 Chiang Y. [122](#)
 Chmelik D. [95](#)
 Cho J. [67](#)
 Chong S. [79](#)
 Choquesillo-Lazarte D. [156](#)
 Chorkendorff I. [53](#), [57](#)
 Chotard J. [12](#), [64](#)
 Christensen M. [23](#), [29](#), [72](#), [74](#),
[82](#), [106](#), [109](#), [110](#), [115](#), [132](#),
[136](#), [163](#), [166](#)
 Christensen S. [23](#)
 Christiansen T. [111](#)
 Chupas P. [66](#), [67](#), [119](#), [122](#)
 Clark I. [106](#)
 Claudon J. [127](#)
 Cléménçon I. [119](#)
 Cliffe M. [19](#)
 Coduri M. [23](#)
 Colaço M. [39](#)
 Colin C. [150](#)
 Collings I. [176](#)
 Colodrero R. [156](#)
 Comotti A. [159](#)
 Conder K. [143](#)
 Confalonieri G. [24](#)
 Connor L. [27](#), [30](#)
 Cooper A. [79](#)
 Costa F. [39](#)
 Costantino F. [97](#)
 Crespi A. [129](#)
 Croguennec L. [12](#), [79](#)
 Cucinotta F. [164](#)
 Cuesta A. [112](#)
 Cuffini S. [95](#)
 Czech M. [180](#)

D

Dadivanyan N. [85](#)
 Dalconi M. [112](#)

Damsgaard C. [53](#), [57](#)
 Daniels L. [25](#)
 Daniš S. [56](#), [131](#)
 Dapiaggi M. [17](#), [24](#), [167](#)
 Darie C. [150](#)
 Daro N. [159](#)
 Darwiche A. [66](#)
 Dashjav E. [75](#)
 Datta K. [26](#)
 Davis M. [168](#)
 Day S. [26](#), [81](#)
 Decottignies D. [119](#)
 Dedryvère R. [121](#)
 Dejoie C. [35](#)
 Deledda S. [136](#)
 Demadis K. [156](#)
 Demirci U. [72](#)
 Deniard P. [18](#)
 Devic T. [181](#)
 Deyneko D. [156](#)
 Diehl F. [119](#)
 Dippel A. [17](#), [29](#), [106](#), [137](#), [155](#)
 Dmitrienko A. [38](#)
 Dmitriev V. [176](#)
 Dominko R. [12](#)
 Dong M. [74](#)
 Dooryhee E. [28](#), [116](#)
 Dorovatovskii P. [87](#)
 Drathen C. [142](#), [157](#)
 Dubrovinskaia N. [179](#)
 Dubrovinsky L. [179](#), [180](#), [182](#)
 Dumlupinar G. [170](#)
 Dumont E. [121](#)

E

Efimov V. [143](#)
 Efimova E. [143](#)
 Egan C. [53](#)
 Eger R. [142](#)
 Ehlers G. [142](#)
 Eikeland E. [158](#)
 Elkāim E. [113](#), [121](#)
 Emerich H. [105](#)
 Emmerling F. [135](#)
 Enseling D. [170](#)
 Ermakova O. [180](#)
 Evans A. [26](#)
 Eymery J. [127](#)

F

Fabry P. [181](#)

Fahim I. [58](#)
 Fajarí L. [40](#)
 Fandaruff C. [95](#)
 Favero M. [112](#)
 Fearn S. [106](#)
 Fécant A. [119](#)
 Fernandez C. [136](#)
 Fernández-Martínez A. [164](#)
 Ferrari G. [112](#)
 Ferreira F. [39](#), [40](#), [169](#)
 Ferrero C. [23](#)
 Fichtner M. [20](#)
 Filinchuk Y. [67](#), [70](#), [163](#)
 Filsø M. [163](#)
 Fink L. [28](#)
 Fiordaliso E. [53](#)
 Fitch A. [24](#), [45](#), [48](#), [50](#), [108](#)
 Flöter E. [152](#)
 Foerst M. [150](#)
 Fojtikova J. [100](#)
 Fonovic M. [98](#)
 Fontaine C. [121](#)
 Fook P. [95](#)
 Foucher D. [113](#)
 Fransen M. [85](#)
 Friedel P. [134](#)
 Frison R. [22](#), [130](#)
 Frontera C. [129](#)
 Frølich S. [55](#), [96](#)
 Fujimura D. [158](#)
 Fujinawa G. [56](#)
 Funakoshi K. [177](#)
 Funnell N. [27](#)

G

Galimberti M. [113](#)
 Galli L. [150](#)
 Galli S. [159](#)
 Galliez K. [18](#)
 Gallington L. [176](#)
 García-Maté M. [117](#)
 Garczarek P. [156](#)
 Gardner J. [142](#)
 Garrido L. [164](#)
 Gateshki M. [24](#), [27](#), [132](#)
 Gavilano J. [141](#)
 Gavryushkin P. [177](#)
 Gérard J. [127](#)
 Gertenbach J. [132](#)
 Geßwein H. [109](#), [115](#)
 Gestin M. [132](#)
 Giacobbe C. [46](#), [159](#)
 Giannopoulou A. [45](#), [50](#)

Gierlotka S. [29](#), [133](#), [180](#)
 Giuseppe C. [130](#)
 Glatthaar S. [115](#)
 Glowacki M. [180](#)
 Gogin A. [86](#)
 Goloveshkin A. [133](#)
 Golub A. [133](#)
 Goodwin A. [19](#), [27](#), [30](#), [141](#),
[142](#), [151](#), [176](#)
 Gozzo F. [45](#)
 Granados-Miralles C. [74](#), [115](#),
[132](#), [166](#)
 Gravereau P. [37](#), [41](#)
 Gray E. [92](#)
 Greenberg E. [180](#)
 Grey C. [66](#), [67](#), [119](#)
 Griffin J. [66](#)
 Gromilov S. [101](#)
 Grosjean A. [159](#)
 Grube E. [68](#)
 Guagliard A. [130](#)
 Guagliardi A. [22](#), [36](#), [46](#)
 Guillou N. [151](#)
 Guionneau P. [159](#), [162](#)
 Gundlach C. [53](#)
 Gunnlaugson H. [120](#)
 Gustafson J. [127](#)
 Guzik M. [136](#)

H

Habermehl S. [37](#)
 Hafsia B. [153](#), [165](#), [166](#)
 Haines J. [176](#)
 Hakim S. [96](#)
 Hakkola S. [161](#)
 Hald P. [131](#)
 Hammer S. [37](#)
 Hannon A. [25](#)
 Hansen B. [68](#)
 Hansen T. [53](#), [91](#), [143](#)
 Hanson J. [116](#)
 Harkera N. [21](#)
 Hartmann T. [28](#)
 Hasa D. [46](#)
 Hasse B. [83](#)
 Hauback B. [20](#), [74](#)
 Havlicek D. [134](#)
 Hayatifar M. [130](#)
 Hayward M. [30](#)
 He G. [134](#)
 Heczko M. [155](#)
 Henry P. [81](#)
 Heussen P. [152](#)

Higo Y. [177](#)
Hill J. [151](#)
Hillman J. [22](#)
Hinrichsen B. [80](#)
Hinterstein M. [7](#)
Hirscher M. [67](#)
Hodeau J. [84](#)
Hoelzel M. [107](#)
Hofmann M. [107](#)
Holm S. [82](#)
Horcajada P. [181](#)
Hrenar T. [46](#)
Hua X. [67](#)
Hudson M. [67](#)
Hull S. [149](#)
Hölsä J. [161](#)
Hörmann C. [87](#)
Haase D. [84](#)

I

Ibáñez R. [94, 96](#)
Ibsen C. [116](#)
Iles G. [67](#)
Iversen B. [17, 23, 29, 63, 106, 110, 120, 131, 154, 155, 158, 161, 163, 168, 171](#)

J

Jacques S. [53](#)
Janeček M. [117](#)
Janik K. [57](#)
Janot R. [64, 163](#)
Javadian P. [69](#)
Jazouli A. [37, 41](#)
Jehnichen D. [134](#)
Jensen A. [70](#)
Jensen K. [17, 29, 106, 109, 110, 115](#)
Jensen S. [68](#)
Jensen T. [64, 67, 68, 69, 70, 71, 73, 74, 118, 163](#)
Jepsen L. [64, 70, 74](#)
Jia C. [65](#)
Jiang L. [86](#)
Jobic S. [18](#)
Johansson K. [41](#)
Johnsen S. [120](#)
Jones G. [48](#)
Jones M. [106](#)
Jooss C. [150](#)
Jorgensen S. [67](#)

Jović O. [46](#)
Juhás P. [47](#)
Julià L. [40](#)
Jung D. [46, 87](#)
Juranyi F. [141](#)
Jüstel T. [170](#)

K

Kadlecová A. [117](#)
Kaganer V. [91](#)
Kai J. [161](#)
Kalinovčić P. [46](#)
Kalvoda L. [93](#)
Kamazawa K. [141](#)
Kaminska A. [180](#)
Kanatzidis M. [149](#)
Kaoua S. [37, 41](#)
Karavassili F. [45, 50](#)
Kareiva A. [170](#)
Karpinsky D. [143](#)
Kaszur Z. [128](#)
Katelnikovas A. [170](#)
Keen D. [30](#)
Kehres J. [53](#)
Keller L. [143](#)
Kenzelmann M. [143](#)
Kern A. [80](#)
Khaled C. [153](#)
Khalyavin D. [142](#)
Kharchenko A. [132](#)
Kheireddinea A. [58](#)
Kichanov S. [175](#)
Kidd P. [132](#)
Kimber S. [24](#)
Klan M. [134](#)
Kleeberg R. [30](#)
Klemradt U. [137](#)
Knapp M. [167](#)
Knox K. [149](#)
Koch R. [97, 129](#)
Kohlmann H. [107](#)
Koike Y. [158](#)
Kojdecki M. [94, 96](#)
Kolarik K. [160](#)
Konopkova Z. [180](#)
Konya T. [56, 158](#)
Korablov D. [70](#)
Korobeynikov M. [153](#)
Kowoll T. [75](#)
Kozlenko D. [13, 175](#)
Krahl T. [135](#)
Kraus F. [142](#)
Kremer J. [142](#)

Krimi S. [37, 41](#)
Kroke E. [178](#)
Kruml T. [155](#)
Kubíčková S. [136](#)
Kucerakova M. [93](#)
Kuhs W. [91](#)
Kuplich L. [39](#)
Kurz S. [97](#)
Kužel R. [56, 99, 117](#)
Kuziora P. [71](#)
Kyncl J. [100, 160](#)

L

Lahoubi M. [144](#)
Laihinen T. [161](#)
Lajaunie L. [121](#)
Lambertin D. [18](#)
Larse S. [3](#)
Larsen H. [161](#)
Lastusaari M. [161](#)
Lathe C. [178](#)
Lausi A. [86](#)
Lazoryak B. [156](#)
Lebraud E. [159, 162](#)
Leemreize H. [55, 116](#)
Lefmann K. [82](#)
Legens C. [119](#)
Leineweber A. [11, 97, 98](#)
Lennie A. [106](#)
Leonardi A. [99](#)
Leoni M. [65, 97, 129](#)
León-Reina L. [117, 156](#)
Leriche J. [12](#)
Leskes M. [67](#)
Létard J. [159](#)
Levelut C. [176](#)
Ley M. [68, 70, 71, 118, 163](#)
Leynaud O. [84](#)
Li X. [41, 107](#)
Lieser G. [109](#)
Likhacheva A. [177](#)
Lima L. [39](#)
Litasov K. [177](#)
Liu H. [119, 170](#)
Lixandrão K. [39](#)
Llewellyn P. [151](#)
Lock N. [106, 110, 163](#)
Losev E. [48](#)
Losilla E. [117, 156](#)
Louër D. [7](#)
Lukin E. [175](#)
Lundegaard L. [154](#)

M

Magioui K. [45](#), [50](#)
Malliakas C. [149](#)
Mamakhel A. [29](#), [131](#), [161](#)
Mandula O. [127](#)
Mankowsky R. [150](#)
Mantlíková A. [136](#)
Manuel P. [142](#)
Marchese L. [164](#)
Marchi M. [113](#)
Marchivie M. [49](#)
Margadonna S. [157](#), [182](#)
Margiolaki I. [45](#), [50](#)
Marinoni N. [113](#)
Markovich V. [135](#)
Marshall W. [179](#)
Martí X. [129](#)
Martineau C. [113](#)
Martinetto P. [84](#)
Martinez F. [180](#)
Martínez-Arias A. [116](#)
Martínez-Casado F. [84](#), [164](#)
Martynova S. [101](#)
Marwa A. [164](#), [165](#)
Masala P. [23](#)
Masciocchi N. [36](#), [46](#), [130](#), [159](#)
Masiello F. [85](#)
Maspero A. [36](#), [130](#), [159](#)
Masquelier C. [12](#), [79](#)
Mastropietro F. [127](#)
Matěj Z. [56](#), [99](#), [117](#), [131](#)
Matějová L. [99](#), [131](#)
Matesanz E. [164](#)
Maurin G. [181](#)
Mauroy H. [20](#), [83](#)
Maury S. [119](#)
Mazzeo P. [45](#)
McCusker L. [35](#), [168](#)
Medarde M. [141](#), [143](#)
Meden A. [58](#)
Meier L. [107](#)
Mena M. [141](#)
Messing M. [170](#)
Michaelis M. [135](#)
Michaelsen C. [83](#)
Miele P. [72](#)
Mikhailenko M. [153](#)
Mikula P. [85](#)
Milata V. [41](#)
Millange F. [151](#)
Minikayev R. [167](#), [180](#)
Miravittles C. [40](#)
Mittemeijer E. [97](#), [98](#), [124](#)
Mogilyanski D. [135](#)

Mohamed B. [152](#)
Moizan V. [119](#)
Molodenskiy D. [86](#)
Monconduit L. [66](#)
Mondieig D. [159](#)
Monecke T. [30](#)
Morcrette M. [12](#)
Moreau P. [121](#)
Morin M. [143](#)
Mortensen A. [166](#)
Moutaabbid H. [58](#)
Moutaabbid M. [58](#)
Mudiyanselage S. [116](#)
Murray C. [81](#), [106](#)
Musalek R. [100](#), [160](#)
Müller R. [135](#)
Møller K. [71](#)
Mönig R. [109](#)
Månsson M. [141](#)

N

Nakamura T. [158](#)
Narygina O. [85](#)
Nazarenko B. [154](#)
Neder R. [19](#), [26](#), [31](#)
Négrier P. [159](#)
Néner G. [85](#), [142](#)
Neurohr C. [49](#)
Nguyen T. [63](#), [64](#)
Nicolin V. [127](#)
Nielsen D. [73](#)
Nielsen M. [181](#)
Nielsen T. [70](#)
Norby P. [108](#)
Norrman M. [45](#), [50](#)
Nouha J. [166](#)
Nue V. [120](#)
Nørby P. [120](#), [168](#)

O

O'Hare D. [27](#)
Oh H. [67](#)
Ohbuchi A. [56](#), [158](#)
Okos A. [150](#)
Oleynikov P. [56](#)
Olivera-Pastor P. [156](#)
Omote K. [86](#)
Osakabe T. [86](#)
Ott H. [141](#)
Oueslati W. [100](#), [123](#), [164](#)
Ouvrard G. [121](#)

Ozawa T. [86](#)

P

Paddison J. [19](#), [142](#)
Pagliari L. [167](#)
Paiva Santos C. [49](#)
Pala Z. [100](#), [160](#)
Palmisano G. [159](#)
Palosz B. [29](#), [133](#)
Palosz W. [133](#)
Papadaki M. [156](#)
Papadakis C. [134](#)
Pardo P. [94](#), [96](#)
Parsiades P. [181](#)
Parker J. [106](#), [176](#)
Paskevicius D. [63](#)
Paskevicius M. [64](#)
Pasternak M. [180](#)
Paszkowicz W. [154](#), [167](#), [180](#)
Patino M. [30](#)
Pattison P. [48](#), [176](#)
Pavese A. [17](#)
Péchev S. [37](#), [41](#), [159](#), [162](#)
Pedroso C. [161](#)
Pein A. [121](#)
Peng F. [54](#)
Peplinski B. [135](#)
Peral I. [112](#)
Perlich J. [134](#)
Perversi G. [72](#)
Petit J. [72](#)
Petit P. [18](#), [121](#)
Petrenko O. [142](#)
Pflaum K. [137](#)
Pinar A. [168](#)
Piszora P. [167](#)
Plaisier J. [86](#)
Plocek J. [134](#), [136](#)
Podgorski D. [47](#)
Podsiadlo S. [167](#)
Pokroy B. [11](#)
Polanski M. [71](#), [73](#), [75](#)
Polatidis E. [124](#)
Pomjakushin V. [141](#)
Pomjakushina E. [141](#), [143](#)
Pop A. [150](#)
Popelková D. [56](#), [99](#)
Popov Z. [177](#)
Porcher F. [113](#)
Porta G. [113](#)
Pospiech D. [134](#)
Potter J. [81](#)
Prado V. [40](#)

Pradon A. [121](#)
 Prakapenka V. [175](#), [180](#), [181](#)
 Proffen T. [30](#)

R

Rabah A. [152](#)
 Radid M. [58](#)
 Rafaja D. [92](#), [95](#), [178](#)
 Ramos-Riesco M. [164](#)
 Rashchenko S. [177](#)
 Ravnsbæk D. [70](#), [122](#)
 Raybaud P. [64](#)
 Rebuffi L. [93](#), [95](#)
 Reiss C. [27](#)
 Resch C. [121](#)
 Reuvekamp P. [142](#)
 Rhaiem H. [123](#), [164](#)
 Ricardo C. [95](#)
 Richter B. [67](#)
 Ritter C. [143](#)
 Rius J. [35](#), [40](#), [129](#)
 Robach O. [127](#)
 Rocha H. [95](#)
 Rodrigues L. [161](#)
 Rodriguez J. [116](#)
 Rodríguez-Carvajal J. [143](#)
 Rodríguez-Cheda J. [164](#)
 Roedern E. [73](#), [118](#)
 Roelsgaard M. [168](#)
 Roijers E. [152](#)
 Rousse G. [12](#)
 Rozenberg G. [180](#)
 Rüegg C. [170](#)

S

Sabelfeld K. [91](#)
 Sadikin Y. [65](#)
 Saha D. [17](#), [29](#)
 Salhamen F. [58](#)
 Salles F. [181](#)
 Sanchez del Rio M. [93](#)
 Sangregorio C. [136](#)
 Santacruz I. [112](#), [117](#)
 Sarkar T. [167](#)
 Sarusie R. [74](#)
 Sato J. [169](#)
 Saura-Múzquiz M. [74](#), [115](#)
 Savenko B. [175](#)
 Scalbert J. [119](#)
 Scaramucci A. [143](#)
 Scardi P. [93](#), [95](#), [99](#)

Scavini M. [23](#)
 Schefer J. [82](#)
 Scheptyakov D. [143](#)
 Schimpf C. [178](#)
 Schluckebier G. [45](#), [50](#)
 Schmahl W. [123](#)
 Schmidt J. [168](#)
 Schmidt M. [37](#), [47](#)
 Schneider J. [123](#)
 Schorr S. [143](#)
 Schouwink P. [65](#), [71](#), [118](#)
 Schumann H. [178](#)
 Schwarz M. [178](#)
 Seger B. [57](#)
 Selma Gutierrez A. [49](#)
 Sepe A. [134](#)
 Serre C. [181](#)
 Sharafutdinov I. [53](#)
 Shatskiy A. [177](#)
 Shekhovtov A. [154](#)
 Shen Y. [110](#)
 Sheppard D. [64](#), [69](#)
 Sheptyakov D. [141](#), [170](#)
 Shiramata Y. [56](#)
 Sikolenko V. [143](#)
 Sillassen M. [57](#)
 Silva T. [39](#)
 Singh A. [82](#)
 Sippel C. [91](#)
 Skapin S. [58](#)
 Skaudžius R. [170](#)
 Skibsted J. [74](#)
 Skrobas K. [29](#), [133](#)
 Smeets S. [35](#)
 Smetana B. [155](#)
 Smrčok L. [41](#)
 Sohn Y. [75](#)
 Somers M. [111](#)
 Sommariva M. [24](#), [27](#), [85](#)
 Song J. [74](#)
 Sozzani P. [159](#)
 Spaldin N. [143](#)
 Stare J. [58](#)
 Stare K. [58](#)
 Stefanovich S. [156](#)
 Stel'makh S. [29](#), [133](#)
 Stewart R. [142](#)
 Stingaciu M. [136](#)
 Stipp S. [96](#)
 Stock S. [55](#)
 Stráská J. [117](#)
 Strasky J. [100](#)
 Stratford J. [66](#)
 Streek J. [12](#), [41](#)
 Strobridge F. [119](#)

Straasø T. [171](#)
 Ståhl K. [111](#)
 Suard E. [79](#)
 Subra-Paternault P. [49](#)
 Sugiyama J. [141](#)
 Sulyanov S. [86](#), [87](#)
 Sun J. [54](#)
 suvorov D. [58](#)
 Suzuki X. [135](#)
 Szilágyi P. [64](#)
 Søndergaard M. [161](#)
 Sørby M. [20](#), [74](#)
 Sørensen H. [96](#)
 Saal P. [107](#)

T

Taddei M. [97](#)
 Tagliazucca V. [65](#)
 Tang C. [81](#), [106](#), [176](#)
 Tang W. [64](#)
 Taulelle F. [113](#)
 Tessier C. [121](#)
 Thomas D. [53](#), [84](#), [170](#)
 Thompson A. [176](#)
 Thompson S. [26](#), [81](#), [106](#)
 Thygesen P. [30](#)
 Tietz F. [75](#)
 Tolochko B. [153](#)
 Tomás F. [96](#)
 Torre Á. [112](#), [117](#)
 Torre F. [94](#)
 Tredici I. [167](#)
 Tridane M. [58](#)
 Trojanova Z. [93](#)
 Troyanchuk I. [143](#)
 Tucker M. [22](#), [27](#), [30](#), [176](#),
[179](#)
 Tumanov N. [67](#)
 Tutuncu G. [116](#)
 Tyrsted C. [17](#), [29](#), [106](#), [109](#),
[110](#), [158](#)

U

Ufer K. [30](#)
 Ulmer U. [20](#)
 Urquiola M. [94](#)

V

Valentini L. [112](#)

Valeš V.	99
Vallcorba O.	35 , 40
Valmas A.	45 , 50
van Beek W.	83
Vaughan G.	21
Vejpravová J.	136
Vennestrøm P.	154
Voinovich D.	46
Volk W.	107
Vrána M.	85
Vratislav S.	93

Z

Zacchini S.	130
Zaludov M.	155
Zhang J.	134
Ziegner M.	75
Zobel M.	19 , 31
Zoń J.	156
Zones S.	168
Zotov N.	124

W

Wagner J.	53 , 57
Wahlberg N.	155 , 171
Walid O.	165
Walter P.	137
Walton R.	25 , 151
Wang Q.	27
Wang Y.	181
Webb C.	92
Webb T.	92
Weidenthaler C.	65
Wenderoth P.	107
Wiaderek K.	66 , 119 , 122
Wiesmann J.	83
Wilhelm H.	22
Wilkinson A.	176
Windmüller A.	31
Winter R.	106
Witek K.	75
Wochner P.	124
Wragg D.	105
Wright J.	21 , 45 , 50

X

Xiang K.	122
Xing W.	122
Xu W.	180
Xu X.	67

Y

Yakavenko A.	116
Yamano A.	56
Yot P.	181
Young C.	30
Yu T.	181
Yusenko K.	101 , 157 , 182

Program

	Sunday 15		Monday 16		Tuesday 17		Wednesday 18
		8h30	Plenary lecture Andreas Leineweber <i>Microstrain Broadening</i>	8h30	Plenary lecture J. van der Streek <i>Accurate and Reliable Molecular Crystal Structures from XRPD and DFT-D: State-of-the-art and Future Directions</i>	8h30	Plenary lecture Denis Kozlenko <i>Neutron Diffraction: Current Achievements at a Long Pulse Neutron Source</i>
		9h30	Coffee	9h30	Coffee	9h30	Coffee
		10h00	MS7 In Memory of J. I. (Ian) Langford	10h00	MS1 Total Scattering Techniques and Disorder MS8 In situ, in operando studies	10h00	MS9 Nanomaterials, surfaces and interfaces MS10 Neutron Structural and Magnetic Scattering
		10h10	MS7 Diffraction line profile analysis, stress, strain and texture MS3 Biological and Molecular Materials	12h00	Lunch Bruker workshop EPDIC Committee closed meeting	12h00	Lunch Rigaku workshop
		12h10	Lunch PANalytical workshop	13h30	MS2 Ab initio Structure Solutions MS11 Structure and properties of functional materials	13h30	MS5 Energy Materials MS12 Diffraction under pressure
13h00 to 17h00	ICCD Workshop <i>Materials Characterization Capabilities Using the Powder Diffraction File</i>	13h40	MS4 Combined Methods for Structure Analysis: Electron diffraction, Powder diffraction & Tomography MS6 Progress in instrumentation	15h30		15h30	Coffee
15h00	Registration	15h40	Posters & Coffee		Posters & Coffee	16h00	Plenary lecture Monica Ceretti <i>Non-stoichiometry in correlated oxide materials studied by in situ diffraction methods</i>
17h00 to 19h00	Opening Ceremony Opening lecture Young Scientist Award Distinguished Powder Diffractionist Award Honorary lecture	17h30	Plenary lecture Boaz Pokroy <i>From studying the structure and microstructure of cry-stals formed in nature, to forming new bio-inspired materials</i>	17h30	Plenary lecture Christian Masquelier <i>X-Rays and Neutrons as essential tools for Lithium battery research</i>	17h00 to 18h00	Closing Ceremony Honorary lecture
		18h30		18h30			
	Welcome Party	19h15	Cultural event AROS	19h00	Conference-Dinner		