NEUTRONS FOR SOCIETY

ESRF

ADD2022

ANALYSIS OF DIFFRACTION DATA IN REAL SPACE

16-21 OCT 2022

GRENOBLE, FRANCE

Book of Abstracts

School

Abstract ID : **118**

Monday 17 Oct, 9:00

Structure of Liquid and Amorphous Materials using Pair-Distribution Function Analysis

Phil Salmon

The atomic-scale structure of liquids and glasses is a prerequisite for understanding their material properties. There is an absence, however, of translational periodicity that leads to the Bragg peaks observed in the diffraction pattern for a crystal. Instead, the diffraction pattern is diffuse, and it is a challenge to solve the structure.

In this talk I will outline the theory necessary for understanding the X-ray and neutron diffraction patterns that are measured for structurally disordered materials, and show how these patterns can be used to obtain real-space structural information in the form of partial pair-distribution functions $g_{\alpha\beta}(r)$ [1,2]. Attention will be paid to multi-component systems, where overlap of the pair-correlation functions means that it is not possible to obtain all of the individual $g_{\alpha\beta}(r)$ from a single diffraction experiment. In favourable cases, however, information can be gained by using multi-pattern techniques that include (i) neutron diffraction with isotope substitution (NDIS), (ii) anomalous X-ray diffraction (AXD), and (iii) a combination of X-ray and neutron diffraction. These methods will be illustrated by case studies taken from recent work at central neutron and X-ray facilities.

Finally, I will introduce the ideas behind structural refinement techniques such as reverse Monte Carlo (RMC) and empirical potential structure refinement (EPSR), where measured diffraction patterns are used to guide in the construction of atomistic models.

[1] H. E. Fischer, A. C. Barnes and P. S. Salmon, Rep. Prog. Phys. **69** (2006), 233.

P. S. Salmon and A. Zeidler, J. Phys.: Condens. Matter **27** (2015), 133201.

P. S. Salmon and A. Zeidler, J. Stat. Mech. (2019), 114006.

Primary author(s) : SALMON, Philip Stephen (University of Bath)

Abstract ID : **143**

Monday 17 Oct, 10:30

Recent and future developments in PDF-land

Simon Billinge

There are recently emerging powerful experimental developments related to atomic pair distribution function (PDF) method and total-scattering studies. At this workshop you will learn in detail about carrying out and applying PDF to your own scientific research, and there will be excellent tutorial talks on this. Therefore, in this talk I will focus on recent technological and methodological developments, and some that are in the pipeline, that are allowing ever richer science to be done. Examples include new spatial and time resolved capabilities and novel approaches to modeling. I will also talk about recent applications of PDF to scientific problems enabled by the new developments. I will also describe recent and upcoming developments in PDF analysis and modeling software that are under development in the group.

Primary author(s) : BILLINGE, Simon (Columbia University + Brookhaven National Laboratory)

Abstract ID : **140**

Monday 17 Oct, 11:30

Single-Crystal Diffuse scattering

Reinhard Neder

Diffuse scattering has been observed for almost as long as any single crystal diffraction, see [1] for a recent review on the subject. Further reviews are found for example in [2-7] and references therein. Diffuse scattering is observed for all classes of crystalline materials, metal alloys, simple inorganic materials, quaiscrystals, molecular structures including protein crystals.

The intensity of the Bragg reflections describes the crystal structure very well with one important limitation. To the Bragg reflections all unit cells look alike. The Bragg reflections thus contain information on the average structure only. Any difference between the unit cells manifests itself in additional, usually weak diffuse scattering between the Bragg reflections. The diffuse scattering may be an almost featureless background or show a pattern of intricate complexity and may onsist of streaks, layers, broad peaks or even curved distributions.

The origin of the structural deviations may be due to dynamic effects such as the thermal movement of atoms or due to static effects. The first effect is commonly termed thermal diffuse scattering, while the second effect is referred to as disorder diffuse scattering.

The static deviations from the average structure can have many different reasons and may be present at different dimensions within the crystal. The deviations may be something as simple as a distribution of two or more atom types at a single site within the unit cell. Very often these local replacements cause a slight static shift of the surrounding atoms and these may be described as small clusters of slightly different structure. In a molecular structure the simplest defects might be a molecule in a slightly different conformation. From these simple defects one can consider a continuous and gradual change to larger objects such as domains with slightly different order or actual disolutions of a guest phase in the host crystal. Other defect types may disrupt the strict periodicity of the crystal on a larger scale such as stacking faults. Commonly the periodicity is maintained within the layers but the layer sequence deviates from a strictly periodic sequence.

Somewhat independent of the actual defect type, we need to consider the distribution of the defects throughout the host structure. Many times the defects are not randomly distributed and the correlations between neighboring defects introduce structure into the diffuse scattering.

In this lecture an overview of defect types, the arrangement of defects and the corresponding diffuse scattering is given. The lecture will describes current measurement, analysis and modelling techniques.

[1] T.R. Welberry, T. Weber, Crystallography Reviews **22**, (2015)

B.T.M. Willis, H. Jagodzinski, F. Frey, J.M. Cowley, J. Gjonnes, P.S. Pershan in Int. Tables for Crystallography Vol B , U. Shmueli (Ed.), IUCR (1993), p. 383

W. Schweika, Springer (1998)

V.M. Nield, D.A. Keen, Oxford University Press (2001)

T.R. Welberry, Oxford University Press (2004)

R.B. Neder, T. Proffen, Oxford University Press (2008)

T.R. Welberry, D.J. Goossens., IUCrJ. **1**, 550 (2014)

Primary author(s) : NEDER, Reinhard (Friedrich-Alexander_universitaet Erlangen-Nuernberg, Germany)

Abstract ID : **138**

Monday 17 Oct, 14:00

PDFgui – a small box modelling platform for nanoscale structure analysis

Emil Bozin

PDFgui is a user-friendly graphical interface built on the PDFfit2 small box modeling engine to fit neutron and X-ray PDF data and extract nanoscale structure information. The easy to use PDFgui environment organizes fits and simplifies many data analysis tasks, such as configuring and carrying out sequential refinements and plotting multiple fits. PDFfit2 is a program as well as a library for real-space refinement of crystal structures. It is capable of fitting a theoretical three-dimensional (3D) structure to atomic pair distribution function data and is ideal for nanoscale investigations. The fit system accounts for lattice constants, atomic positions and anisotropic atomic displacement parameters, correlated atomic motion, and experimental factors that may affect the data. The atomic positions and thermal coefficients can be constrained to follow the symmetry requirements of an arbitrary space group. PDFfit2 and PDFgui are freely available [1]. In this talk, the PDFgui concept and layout as well as essential capabilities will be presented. To exemplify the small box analysis as applied to bulk systems featuring nanoscale heterogeneities, a brief illustration of a recent hidden local symmetry breaking detection in a high performance thermoelectric system will be shown [2]. PDFgui functionality and typical use cases, such as co-refinement of multiple datasets, phase analysis, sequential refinements of variable length scales, temperature & composition, will be demonstrated during the followup hands-on tutorial. .

[1] “PDFfit2 and PDFgui: computer programs for studying nanostructure in crystals”, C L Farrow et al., J. Phys.: Condens. Matter **19** 335219 (2007)

“Hidden local symmetry breaking in silver diamondoid compounds is the root cause of ultralow thermal conductivity”, H. Xie et al., Adv. Mater. **34** 2202255 (2022)

Primary author(s) : BOZIN, Emil (Brookhaven Natl Lab)

Abstract ID : **144**

Monday 17 Oct, 14:30

DiffPy-CMI - a software toolbox for real-space structure analysis and Complex Modeling

Simon Billinge

This presentation and the associated hands-on tutorial will introduce DiffPy-CMI, a software for structure analysis from experimental atomic Pair Distribution Function (PDF) and for Complex Modeling [1, 2]. DiffPy-CMI (Complex Modeling Infrastructure) has been developed to handle ill-posed inverse problems, where diffraction experiments do not provide enough signal to determine complicated structures or nanostructures. To overcome this problem, we use a Complex Modeling approach [3] which allows users to combine additional experimental or theoretical inputs and uses them all together in a common optimization routine. DiffPy-CMI is a flexible and extensible program allowing user to create such models tailored for the specific knowledge about the material under study. DiffPy-CMI runs on Linux and Mac operating systems and is primarily written in Python with computationally intense parts coded in C++. It can also be run on windows using the Windows Linux Subsystem (WSL). In the big picture DiffPy-CMI provides several ways of representing atomic structures, a set of forward calculators (e.g., PDF, bond valence sums, powder and single crystal diffraction), and finally a fit-manager to define and run multi-input refinements. The fits can be conducted with short Python scripts or within the Jupyter Notebook interactive environment. In addition to Complex Modeling, DiffPy-CMI also enables more subtle PDF refinements which are not possible in PDFgui [4] - for example PDF fits of non-periodic small clusters or of molecular crystals with rigid structure units. The software provides access to internal simulation routines, which can be tweaked or extended, and thus permits rapid implementation of new ideas and more accurate models. We will demonstrate the capabilities of DiffPy-CMI on a series of science cases, starting from simple forward calculations and following up with PDF fitting examples that go beyond PDFgui.

[1] P. Juhás, et al., Acta Crystallogr. A 71 (2015), 562-568.

DiffPy-CMI is available at https://www.diffpy.org.

S. J. L. Billinge, I. Levin, Science 316 (2007), 561-565.

C. L. Farrow et al., J. Phys: Condens. Mat. 19 (2015), 335219.

Primary author(s) : BILLINGE, Simon (Columbia University + Brookhaven National Laboratory); JUHAS, Pavol (Brookhaven National Laboratory); Mr. TAO, Songsheng (Department of Applied Physics and Applied Mathematics, Columbia University)

Abstract ID : **108**

Monday 17 Oct, 15:00

Investigating short-range magnetic correlations in real space with magnetic pair distribution function analysis

Benjamin Frandsen

Short-range magnetic correlations play a key role in a wide variety of material systems, ranging from quantum materials, such as geometrically frustrated magnets, to technologically applied materials, such as magnetocalorics. Quantitatively characterizing these correlations is necessary to gain a complete understanding of these types of materials, but conventional techniques based on magnetic diffraction fail due to the short-range nature of the correlations of interest. Recently, magnetic pair distribution function (mPDF) analysis has emerged as a promising method for studying short-range magnetic correlations by Fourier transforming the magnetic scattering into real space, similar to the more familiar atomic pair distribution function method. mPDF analysis has been applied successfully to numerous magnetic materials, including geometrically frustrated magnets, strongly correlated electrons systems, magnetic thermoelectrics, multiferroics, and more. In this talk, I will introduce the mPDF method, discuss its application to representative materials, and provide an overview of the software tools available for mPDF analysis.

Primary author(s) : FRANDSEN, Benjamin (Brigham Young University)

Abstract ID : **136**

Monday 17 Oct, 16:00

RMCProfile: Local structure of crystalline to amorphous materials

Matt Tucker

Many of the useful materials that make modern life possible are crystalline. Quartz keeps our watches on time, perovskites are widely used in consumer electronics and solid oxide fuel cells may help to power the future.

The importance of local structure and disorder in crystalline materials is being recognised more and more as a key property of many functional materials. From negative thermal expansion to solid state amorphisation and the 'nanoscale' problem to improved fuel cell technology, a clear picture of the local atomic structure is essential to understanding these phenomena and solving the associated problems.

Total scattering, an extension of the powder diffraction method, is increasingly being used to study crystalline materials. The unique combination of Bragg and diffuse scattering can be used to determine both the average structure and the short-range fluctuations from this average within a single experiment. To maximise the structural information from such data, three-dimensional atomic models consistent with all aspects of the data are required.

RMCProfile [1] expands the reverse Monte Carlo (RMC) modelling technique [2] to take explicit account of the Bragg intensity profile from crystalline materials. Analysis of the RMCProfile-generated atomic models gives more detailed information than is available directly from the data alone. We will give several examples where RMCProfile has been used to successfully study the structure and disorder of crystalline materials to illustrate its potential. Also, since the original RMC technique was designed to study amorphous materials, we will give examples where RMCProfile has been used to model amorphous structures that derive from crystalline materials.

[1] see www.rmcprofile.org; M G Tucker, D A Keen, M T Dove, A L Goodwin and Q Hui, J. Phys. Condens. Matter 19, 335218 (2007)

R L McGreevy amd L Pusztai, Mol. Simul. 1, 359 (1988)

Primary author(s) : TUCKER, Matt (ORNL); PLAYFORD, Helen (ISIS Neutron and Muon Source)

Abstract ID : **141**

Monday 17 Oct, 16:30

EPSR & Dissolve - Data-driven structural modelling of total scattering data

Tristan Youngs

The study of disordered materials such as liquids and glasses through neutron or x-ray techniques presents an interesting challenge since, due to the presence of only local order (< 1 nm) in these materials, only diffuse scattering prevails. Searching for, or generating model analogues that match this "order in disorder" present in the structure of real systems is normally required to make any kind of scientific interrogation. This is the goal of the Empirical Potential Structure Refinement (EPSR) [1] and Dissolve [2] codes.

Both EPSR and Dissolve rely on a full, atomistic simulation (Monte Carlo and/or molecular dynamics) of a target system and its constituent molecules and moieties within the context of a "realistic" forcefield describing the interactions between atoms. While simulations utilising off-the-shelf forcefields typically do not reproduce experimentally-measured structure factors, they act as a useful starting point for further refinement. Critically, the provision of experimental scattering data allows both codes to modify the interatomic potentials provided and drive the simulated system towards better agreement with the real-world one. This data-driven approach to the modelling of total scattering data has successfully been applied to a multitude of disordered systems covering liquids, liquid mixtures, and glasses, and is increasingly being used to study complex disordered materials such as gases and liquids confined in porous materials, polymers in solution, and self-assembled systems such as aqueous micelles.

Here I will give an overview of the techniques and approaches involved, their advantages, limitations and challenges, and discuss some real-world examples.

[1] Soper, *Mol. Phys.* **99**, 1503 (2001)

Youngs, *Mol. Phys.* **117**, 3464 (2019)

Primary author(s) : YOUNGS, Tristan; BOWRON, Daniel (UK Research and Innovation, Science and Technology Facilities Council, ISIS Neutron and Muon Facility)

Abstract ID : **139**

Tuesday 18 Oct, 9:00

Refinement of Magnetic Diffuse Scattering Data

Joe Paddison

I will discuss techniques for refinement of magnetic diffuse scattering data, and the real-space information they can provide about magnetic materials such as spin liquids, spin ices, and skyrmion crystals. I will introduce the computer programs Spinvert and Spinteract, which can be used to estimate the short-range magnetic correlations and the magnetic interactions that drive them, respectively. I present several examples to demonstrate the capabilities of the suite of programs: fitting to powder and single-crystal diffuse-scattering data, predicting single-crystal diffuse-scattering patterns given powder data, and parametrising spin Hamiltonians of magnetic materials using magnetic diffuse scattering data.

Primary author(s) : PADDISON, Joe (Oak Ridge National Laboratory)

Abstract ID : **119**

Tuesday 18 Oct, 9:30

DISCUS, Simulation and refinement of disordered crystal structures

Reinhard Neder

Kristallographie und Strukturphysik,Friedrich-Alexander-Universität Erlangen-Nürnberg, Staudtstr. 3, 91058 Erlangen

DISCUS is a program that can simulate crystal structures and can calculate the orresponding diffraction pattern[1]. Its scope includes the possibility to simulate perfect crystal structures, as well as disordered structures. The program includes several toolboxes to introduce defects into the crystal structure. The strength of the program is the nearly unlimited flexibility that it offers to the user. One can use the program to simulate individual atoms, molecules, small clusters, finite sized nanoparticles or crystals that are essentially infinite in size. Into each of these structures many different defects can be introduced via a set of tools integrated into the program.that still as an average periodic crystal structure, or a complex core/shell nanoparticles as well as a glass like structure without periodicity.

The tools to create disorder include basic options like the manipulation of individual atoms and extended tools to manipulate the crystal at large. These tools include short range order concepts to distribute different atom species or to distribute displacement correlations throughout the crystal. Empirical potential functions allow to introduce local distortions to the structure. Another tool builds stacking faults. These can be created as growth faults or use a short range order mechanism to build faults with more complex layer sequences. A new companion program allows the use of abstract generators to create essentially any stacking fault sequence. DISCUS uses an abstract domain concept to incorporate defects into a host structure. These defects might be anything from an individual atom, a small cluster, a guest crystal with regular or irregular internal host-guest surface or a set of molecules on top of a surface. The domains themselves may be subject to a short range order distribution. Finally, modulated structures can be simulated with the use of displacement or density waves. To build finite crystals, options exist to create crystals limited by a suitable surface.

DISCUS calculates single crystal diffraction pattern of as well as powder diffraction pattern, the pair distribution function (PDF), and the 3D-PDF.

The DISCUS program suite [2] includes two generic optimizer sections to refine disordered crystal structures with respect to experimental data. The DISCUS suite is available for Linux, Mac and Windows. The programm includes an MPICH option to allow fast parallel refinement on multiple core architectures or supercomputer frames.

A set of interactive teaching pages is available to introduce disorder diffraction concepts [3].

[1] R.B. Neder, T. Proffen, Diffuse Scattering and Defect Structure Simulation, Oxford (2008)

[2] DISCUS is available on https://github.com/tproffen/DiffuseCode

[3] DISCUS Teaching pages available on https://www.icsp.nat.fau.eu/neder-group/ (Under revision)

[4] K. Page, T.C. Hood, Th. Proffen, R.B. Neder, J. Appl. Cryst **44**, 327 (2011)

Primary author(s) : NEDER, Reinhard

NEUTRONS
FOR SOCIETY
ESRF
ADD2022
ANALYSIS OF DIFFRACTION DATA
IN REAL SPACE
16-21 OCT 2022
GRENOBLE, FRANCE

Abstract ID : **137**

Tuesday 18 Oct, 10:00

3D-ΔPDF: Pair distribution function analysis for single crystals

Arkadiy Simonov

This tutorial will be focused on understanding disorder in single crystals using diffuse scattering. In particular I will introduce the Three-Dimensional Difference Pair Distribution Function (3D-ΔPDF) method for analyzing diffuse scattering from single crystals and the program Yell which can perform 3D-ΔPDF refinements.

Primary author(s) : SIMONOV, Arkadiy

Abstract ID : **115**

Tuesday 18 Oct, 12:15

Hybrid Photon Counting X-Ray Detectors: from Basic Functionality to Advanced Operation during X-Ray Diffraction Experiments

Dubravka Sisak-Jung

Hybrid photon counting (HPC) X-ray detectors are crucial components for cutting-edge research at synchrotrons and in laboratories. In short, HPC X-ray detectors provide (i) noise-free detection and readout, (ii) high-quantum efficiency over a wide X-Ray energy range, and (iii) advanced acquisition functionality for versatile experiments at up to kilohertz image rates.

During this talk, we will address the core components of latest-generation HPC detectors, such as the PILATUS3 and EIGER2, explaining their core building blocks as well as their respective functionality. We will highlight key aspects to consider before, during, and after the experiment, to ensure the best possible data quality.

Primary author(s) : Dr. SISAK-JUNG, Dubravka (DECTRIS Ltd.)

Conference

Abstract ID : **110**

Wednesday 19 Oct, 14:45

PDF methods in materials chemistry

Andrew Goodwin

This talk will give an overview of various applications of PDF methods in Materials Chemistry. Examples will be drawn from across the field, including metal–organic frameworks, frustrated magnets, battery materials, and oxide ceramics. The talk will include discussion of the pros and cons of single-crystal vs powder PDF methods, and also the different emphases of reciprocal space (total scattering) vs real space (PDF) representations.

Primary author(s) : Prof. GOODWIN, Andrew (University of Oxford)

Abstract ID : **121**

Wednesday 19 Oct, 16:00

Local and extended structuring in not-so-crystalline molecular solids

Max Terban

One of many benefits of real-space analysis is to provide a different vantage point from which to analyze our diffraction/scattering data. Certain features of the structure are better emphasized in real-space. This provides opportunities to test different hypotheses about parts of the structure, and how they change, even when a complete structural model is unknown or not well defined. In this talk, I will discuss different case studies for using PDF data to study complex molecular materials — e.g. thiophosphate anions with dynamic disorder and macromolecular chain structures forming heterogeneous aggregations. I will show how to disambiguate aspects of the structuring over different length-scales. Importantly, emphasis will be placed on comparing total scattering features with their real-space analogues to help build intuition for future PDF endeavors.

Primary author(s) : TERBAN, Maxwell

Abstract ID : **83**

Wednesday 19 Oct, 16:45

From Total Scattering to Total Understanding: Structure-Functionality Relationships in Scheelite-Type Oxides

Bryce Mullens

The development of carbon-neutral energy-generation and storage is critical to combatting climate change. Various technologies are currently being developed for sustainable energy generation, such as next-generation ion conductors for solid-oxide fuel cells (SOFCs), industrial catalysts for sustainable processing, and materials capable of safely storing radioactive waste. Scheelite-type *AB*O4 materials have become a focus for these technological advances, with RbReO4 emerging as a potential solid electrolyte, Bi3FeMo2O12 as a viable oxidation catalyst, and TlTcO4 as a model for highly mobile nuclear fission products. Paramount to the development of these technologies is a deep understanding of their structure-functionality relationships. In this work, we have investigated materials that show unusual temperature dependent structural properties and use total scattering techniques to fully understand the structural origins of such behavior.

RbReO4 undergoes a continuous phase transition from *I*41/*a* to the true *I*41/*amd* scheelite aristotype upon heating. This phase transition is particularly important as it changes the number of possible interstitial sites, potentially leading to higher ionic conductivity. Rietveld refinements using synchrotron X-ray diffraction data shows an anomalous reduction in the Re-O bond lengths upon heating towards the phase transition temperature. This is unexpected, as the *B*O4 scheelite tetrahedra are traditionally considered rigid with ‘fixed’ *B*-O bond distances. Combining synchrotron X-ray diffraction and X-ray total scattering data, we uncovered a unique symmetry-lowering process on the local scale involving incoherent tetrahedra rotations. By manipulating the size of the *A*-site cation, local scale disorder can be tuned to tailor the physical properties of the material [1].

Bi3FeMo2O12 is a rare example of a transition metal oxide that undergoes a symmetry-lowering 2:1 cation ordering upon heating. Synchrotron X-ray and neutron powder diffraction demonstrate that this is a consequence of a first-order tetragonal-to-monoclinic phase transition that occurs at temperatures below 600 ℃. Neutron pair distribution function analysis revealed that the transition does not involve a rearrangement of the cation sublattice but showed that the Bi3+ 6*s*2 lone pairs are stereochemically active in both phases. The observed phase transition is a result of changes in the correlation length of the of the Bi3+ 6*s* electrons from short range in the tetragonal structure to long range in the monoclinic structure. This is then used to understand the magnetization of the different phases [2].

TlReO4 is a rare example of a non-magnetic oxide displaying a re-entrant phase transition. The symmetry changes from tetragonal *I*41/*a* to monoclinic *P*21/*c*, and then back to tetragonal *I*41/*a* upon heating. Using neutron total scattering, we describe this behavior in terms of the correlation length of the Tl+ 6*s*2 lone pairs. Whilst the long-range average structure experiences emphanitic behavior (that is, the emergence of a lower-symmetry phase upon heating), the local structure is best fitted with monoclinic distortions to the unit cell due to the Tl+ lone pairs. This study presents a possible method of tuning the energy landscape of lone pair-containing functional materials [3].

[1] Marlton, F. *et al.*; Tetrahedral Displacive Disorder in the Scheelite-Type Oxide RbReO4. *Inorg. Chem.*, In Press.

Saura-Múzquiz, M. *et al.*; Cation and Lone Pair Order-Disorder in the Polymorphic Mixed Metal Bismuth Scheelite Bi3FeMo2O12. *Chem. Mater.*, To be Submitted.

Saura-Múzquiz, M. *et al.*, Understanding the Re-Entrant Phase Transition in a Non-Magnetic Scheelite. *J. Am. Chem. Soc.*, https://doi.org/10.1021/jacs.2c05620.

Primary author(s) : MULLENS, Bryce (The University of Sydney / University Paris Saclay); MARLTON, Fred (Aarhus University, Chemistry); Dr. SAURA-MUZQUIZ, Matilde (Universidad Complutense de Madrid); BALDINOZZI, gianguido (Université Paris-Saclay, SPMS, Centralesupelec CNRS); Dr. ZHANG, Zhaoming (Australian Nuclear Science and Technology Organisation); Prof. KENNEDY, Brendan (The University of Sydney)

Abstract ID : **71**

Wednesday 19 Oct, 17:10

Probing hidden order in ferroelectric oxide thin films with single crystal diffuse X-ray scattering

Joohee Bang

Ferroelectric thin films have attracted great attention for its rich applications in energy-efficient electronic devices because of their relevant physical properties such as high dielectric constants, electrically switchable polarization, and high piezoelectric coefficients [1]. In fact, the growing demand for miniaturized microelectronics has inspired diverse research efforts towards the engineering of ferroelectric properties and domain architectures in the ultrathin regime [2]. Thus, comprehending the structural and electrical properties of ferroelectric thin films on the nanoscale became crucial. Recently, a lot of effort has been put into studying ferroelectric oxide superlattices with complex topologies such as long-range vortex-antivortex arrays of polarization [3]. These works have called for an in-depth structural investigation of the superlattice structures, since the orientation and arrangement of ferroelectric domains define the macroscopic ferroelectric properties in ferroelectric thin films. Here, we report on a newly discovered local order state in superlattices consisting of ferroelectric lead titanate and dielectric strontium titanate using a complete three-dimensional diffuse X-ray scattering data analyzed with 3D-ΔPDF method [4]. The data was collected with single crystal diffuse X-ray scattering technique, which, to the best of our knowledge, was used for the first time to study local order in single crystalline thin films. This work will not only contribute to gaining useful insights on structure-property correlations of ferroelectric oxide superlattices, but also lay groundwork for developing a novel non-disruptive solid-state characterization technique for analyzing local structures of thin films.

[1] Setter, N., et al. 2006

Fong, Dillon D., et al. 2004; Schlom, Darrell G., et al. 2007

Yadav, A. K., et al. 2016; Damodaran, A. R., et al. 2017

Weber, T., Simonov, A. 2012

Primary author(s) : Ms. BANG, Joohee (ETH Zurich); Dr. STRKALJ, Nives (Cambridge University); Mr. SAROTT, Martin (ETH Zurich); Prof. TRASSIN, Morgan (ETH Zurich); Dr. WEBER, Thomas (ETH Zurich)

NEUTRONS
FOR SOCIETY
ESRF
ADD2022
ANALYSIS OF DIFFRACTION DATA
IN REAL SPACE
16-21 OCT 2022
GRENOBLE, FRANCE

Abstract ID : **84**

Wednesday 19 Oct, 17:35

Emergent Electronic and Phonon Modes from Correlated Disorder

Nikolaj Roth

Disorder in crystals is often far from random, and in some cases the local correlations of disorder can be controlled. It is shown how crystals with identical average crystal structures, but different types of correlated disorder can have different electronic and phonon band structures. It is further shown that by changing the type of disorder from random to correlated, it is possible to open band gaps and tune the delocalization of modes, allowing for drastic changes to electronic properties. Bragg diffraction patterns are not enough to identify a structural phase when disorder is at play, as phases with widely different properties can have identical Bragg diffraction intensities. Diffuse scattering is needed to identify phases with disorder. Control over correlated disorder allows a new handle for tuning materials properties.

Primary author(s) : ROTH, Nikolaj (University of Oxford)

Abstract ID : **117**

Thursday 20 Oct, 8:30

A pedagogical journey in search of hydrogen disorder with RMCProfile analysis of X+n data from hydrogrossular

David Keen

The structure of fully hydrated grossular, Ca3Al2[(OH)4]3, contains an unusual arrangement of four O-H bonds within each tetrahedral cavity when all SiO4 in the anhydrous form are substituted for (OH)4. Neutron and x-ray total scattering from a powdered deuterated sample were measured and modelled using RMCProfile to investigate the local arrangement of this O4D4 cluster [1]. This showed that, other than the consequences of a correctly determined (and longer) O-D bond length, there is little to suggest that the O4D4 structure is locally significantly different from that expected based on the average structure determined solely from Bragg diffraction.

This talk will therefore concentrate on the X+n total scattering data analysis process, which proved very instructive, provided a few surprises, and will hopefully be of help to others using total scattering/PDF data to understand disorder in crystalline materials.

[1] D A Keen, D S Keeble and T D Bennett. Phys. Chem. Miner. 45 (2018) 333-342

Primary author(s) : Prof. KEEN, David (ISIS Facility, Rutherford Appleton Laboratory)

Abstract ID : **85**

Thursday 20 Oct, 9:15

Exploring fundamental aspects of the structural organization in weberite-type tantalate oxides using neutron total scattering technique.

Igor Gussev

The total scattering technique provides key information about the periodic long-range structure and local atomic correlations, essential to unravel underlying defects and structural disorder. Understanding how complex oxides disorder is critically important for many energy-related applications that require materials operating in harsh environments (high pressure, temperature, and radiation fields).

We used neutron total scattering and X-ray diffraction to study a series of weberite-type tantalate oxides (RE3TaO7, RE= rare earth). Weberite-type oxides are structurally related to fluorite and their chemical flexibility and ability to incorporate atomic substitutions can produce systems relevant for nuclear waste management, atomic transport, or magnetic applications. Modeling of neutron total scattering data across all material's length scales demonstrated that short-range correlations differ from the respective long-range atomic organizations: The Q-space analysis revealed three different long-range symmetries, whereas r-space correlations displayed a continuous behavior across the entire compositional series, even extending to the fully disordered defect-fluorite structure. This can be explained by the change in different tilt systems and polyhedra distortions that increase continuously with cation size mismatch. The long-range structures are the configurational average of the local sub-nanodomains; the existence of phase transformations across phase boundaries between three structural families is related to a change in the tilt system in one case and the crossing of a critical distortion level in the other. This complex multiscale disordering behavior can explain the different properties of these systems and, in particular, their varying amorphization resistance to ion irradiation.

Primary author(s) : Mr. GUSSEV, Igor (University of Tennessee)

Co-author(s) : Dr. BALDINOZZI, Gianguido (Université Paris-Saclay); Dr. O'QUINN, Eric (University of Tennessee); Dr. LANG, Maik (University of Tennessee); Dr. NEUEFEIND, Jörg (Oak Ridge National Laboratory)

NEUTRONS FOR SOCIETY
ESRF
ADD2022
ANALYSIS OF DIFFRACTION DATA IN REAL SPACE
16-21 OCT 2022
GRENOBLE, FRANCE

Abstract ID : **94**

Thursday 20 Oct, 9:40

Solving atomic structures by combining analysis of PDF pattern with DFT calculations in machine learning enhanced global optimization

Wilke Dononelli

Determination of crystal structures of nano-crystalline, quantum-crystalline, or amorphous compounds is a great challenge in solid states chemistry and physics. Structural analysis using atomic pair distribution function (**PDF**) of X-ray or neutron total scattering data has the potential to become the most efficient method in this field. Unfortunately, for structure refinements using this method, an initial starting model for the atomic positions is needed, but not available in many cases. To solve this problem, we have recently introduced an algorithm [1] that is able to determine the crystal structure of an unknown compound by means of an on-the-fly trained machine learning (**ML**) model that combines density functional calculations (**DFT**) with comparison of calculated and measured PDFs for global optimization. In our original work, we showed, that the algorithm is able to predict even meta-stable point defects in spinel structures.

Here, we will give a short introduction of the method followed by a case example. $H_2W_2O_7$ and $D_2W_2O_7$ are a metastable material synthesized via selective etching of the Aurivillius-related $Bi_2W_2O_9$ [2] with HCl and DCl, respectively. As shown by Wang et al. [3] this material has the potential to be used as an electrode for high-power proton-based energy storage. Due to the meta-stable nature of the material global optimization of the atomic structure relying on DFT calculations leads to a wrong layer structure. Only combining PDF measurements from X-ray and neutron scattering with DFT calculations leads to the correct layer structure similar to Aurivillius structure of the precursor.

[1] M. Kløve, S. Sommer, B. B. Iversen, B. Hammer and W. Dononelli, Solving atomic structures from PDF patterns with machine learning enhanced global optimization, 2022, submitted. preprint: http://www.quantumchemistry.eu/dftpdf/

N. Lefeld, M. M. Murshed, P. Bottke, Th. M. Gesing, Synthesis and characterizations of $H_2W_2O_7 \cdot nH_2O$ layered tungstates hosting hydrogen storage and conduction. 16th European Conference on Solid State Chemistry, 23. - 26.7.2017 Glasgow, UK.

Wang, R., et al, Fast Proton Insertion in Layered $H_2W_2O_7$ via Selective Etching of an Aurivillius Phase. Adv. Energy Mater. 2021, 11, 2003335.

Primary author(s) : Dr. DONONELLI, Wilke (University Bremen, MAPEX Center for Materials and Processes and Bremen Center for Computational Materials Science)

Co-author(s) : KLØVE, Magnus (Center for Integrated Materials Research, Department of Chemistry and Interdisciplinary Nanoscience Center (iNANO), Aarhus University); Mr. LEFELD, Niels (Universität Bremen, Chemische Kristallographie fester Stoffe, Institut für Anorganische Chemie und Kristallographie); Prof. GESING, Thorsten M. (Universität Bremen, Chemische Kristallographie fester Stoffe, Institut für Anorganische Chemie und Kristallographie); Prof. IVERSEN, Bo B. (Center for Integrated Materials Research, Department of Chemistry and Interdisciplinary Nanoscience Center (iNANO), Aarhus University)

Abstract ID : **64**

Thursday 20 Oct, 10:05

Symmetry-Adapted Pair Distribution Function Analysis

Tobias Bird

Symmetry-Adapted Pair Distribution Function Analysis (SAPA)[1] is a novel technique for obtaining information on local dynamics and disorder from pair distribution function (PDF) data. In the SAPA method, the crystal structure is expanded to a supercell of a given size and then broken down into a symmetry-mode basis using the *ISODISTORT* online software. Using the *TOPAS* command line functionality, groups of modes transforming as the same irreducible representation can be tested in turn, in order to find the modes most responsible for any deviation of the local structure from the average. With the python programming language, this technique can be performed as an automated process. Using this method, it has been possible to elucidate the underlying symmetry of the successive ferroelectric phase transitions in $BaTiO_3$[2] and have highlighted the importance of structural flexibility in determining the range and magnitude of negative thermal expansion in ReO_3[3] and related structures[4].

[1] T. A. Bird, A. Herlihy and M. S. Senn, *J. Appl. Cryst.*, **54** (2021), 1514-1520

[2] M. S. Senn, D. A. Keen, T. C. A. Lucas, J. A. Hriljac and A. L. Goodwin, *Phys. Rev. Lett.*, **116** (2016), 207602

[3] T. A. Bird, M. G. L. Wilkinson, D. A. Keen, R. I. Smith, N. C. Bristowe, M. T. Dove, A. E. Phillips and M. S. Senn, *Phys. Rev. B*, **104** (2021), 214102

[4] T. A. Bird, J. Woodland-Scott, L. Hu, M. T. Wharmby, J. Chen, A. L. Goodwin and M. S. Senn, *Phys. Rev. B*, **101** (2020), 064306

Primary author(s) : Dr. BIRD, Tobias (Diamond Light Source)

Co-author(s) : Dr. CHATER, Philip (Diamond Light Source); Dr. SENN, Mark (University of Warwick)

Abstract ID : **116**

Thursday 20 Oct, 10:55

A nanoscale view of natural and engineered cements

Alejandro Fernández Martínez

Calcium silicate hydrates (C-S-H) are the main binding phase of Portland cement. In spite of more than one century of intensive use, mechanistic details about the nucleation and growth of these hydrates remain elusive. Indeed, the study of nucleation from solution is a difficult experimental task given the nanoscopic sizes of the first nuclei and their short lifetimes. The classical view of the nucleation process is that depicted by the classical nucleation theory, by which the first nuclei formed already have the atomic structure of the final crystals. It has been only in recent years that deviations from this theory have been reported for many mineral phases, which has resulted in what is known as 'non-classical' nucleation pathways in which nanoparticulated or amorphous intermediates are important players during the nucleation process. A study of non-classical nucleation pathways of C-S-H performed using in situ X-ray PDF methods will be reported during the first part of this presentation. Similarities to structural characteristics of natural cements (biominerals) will be highlighted.

In the second part, recent advances in our understanding of the structure of C-S-H and of adsorbed water films will be presented. C-S-H is a disordered, nanocrystalline phase which exhibits variable stoichiometry. This has prevented accurate crystallographic descriptions of its structure, which has also resulted in animated debates in the literature. Recent work seems to converge towards a picture where a defective-tobermorite model could serve to explain most of the structural and mechanical properties of this nanoscopic phase.

Primary author(s) : ZHAKIYEVA, Zhanar; BESSELINK, Rogier (ISTerre, CNRS & Univ. Grenoble Alpes); BUREAU, Sarah (ISTerre, CNRS & Univ. Grenoble Alpes); FINDLING, Nathaniel (ISTerre, CNRS & Univ. Grenoble Alpes); MAGNIN, Valerie (ISTerre, CNRS & Univ. Grenoble Alpes); LA BELLA, Michela (ESRF & ISTerre, CNRS & Univ. Grenoble Alpes); GIACOBBE, carlotta (ESRF); GALLINGTON, Leighanne (APS-ANL); DEJOIE, Catherine (ESRF); VAN DRIESSCHE, Alexander; FISCHER, Henry; CUELLO, Gabriel Julio; FERNANDEZ-MARTINEZ, Alejandro (ISTerre, CNRS & Univ. Grenoble Alpes)

Abstract ID : **62**

Thursday 20 Oct, 11:40

Structural Role of Titanium in Glass and Glass Ceramic Materials

Esther Girón Lange

Titanium glasses were studied aiming a better understanding of the nucleation process in glass and glass-ceramic materials. Two species of glass, namely a Phosphate glass containng Titanium and Niobium, TiO_2-NbO_2-P_2O_5, and a Spinel glass-ceramic, were measured using neutron diffraction at the D4c instrument at the Institut Laue-Langevin (ILL) and x-ray diffraction at the ID15a beamline at the European Synchrotron ESRF. The analysis of their pair distribution functions (PDF) following the method described by Fischer et al. resulted on the preliminary determination of the distances between pairs of atoms and their coordination numbers. Numerous consistency checks are performed during the data processing and analysis to indicate the reliability of these results. In addition to these systems more samples of the same families, i.e. the Phosphate and the Spinel, are being prepared with varying concentrations and annealing stages to extend and complement the analysis.
Nucleation and crystal growth within amorphous materials are of increasing interest among industry due to the potential versatility of their designs. Titanium glasses are important because the presence of this metal has been observed to play a structural role on the crystal growth process. The goal of this research is to develop a model that explains how Titanium affects the crystallisation taking place within the glass in order to effectively design and produce new glass-ceramics. However, the study of glasses is not easy and careful manipulation of the measured data is required in order to identify the differences on the structure of the materials. In this study, the complementary of x-rays and neutrons together with the negative neutron scattering length of Titanium are exploited in order to maximise the information extracted from the data. Results from the two families will be presented, comparing the neutron and x-ray diffraction results, explaining the key steps on the data processing and pointing the main features that can be extracted from the data.

Primary author(s) : GIRON LANGE, Esther

Abstract ID : **100**

Thursday 20 Oct, 12:05

Probing the structural and dynamical properties across the metamictization process in v-SiO2

Erica Alfinelli

The v-SiO_2 is the most widespread basis for all the glasses which can be found in plenty of fields.
Despite the large usage, there are still open questions on its structure and, more important, on the atomic rearrangements after being exposed to external perturbations such as strong radiation fields.
Recent experiments have shown that the strong x-ray beam of brilliant synchrotron sources activate atomic movements via radiolytic processes. In the phenomenon the photon creates a photoelectron which has sufficient energy to break atomic bonds and makes the nearest neighbours to rearrange and change the local configuration [1].
We have investigated this process by means of the X-ray Photon Correlation Technique (XPCS) which is based on the correlation of intensity data and it is sensitive to the density fluctuations providing information on the atomic motions. At the same time we collected also the partial diffraction pattern (the First Sharp Diffraction Peak (FSDP)) of the sample thanks to the extended 2D Eiger4M detector placed ~2 m downstream from the sample stage.
I will show how the metamictization process is evident from the gradual decrease in the intensity and broadening of the FSDP while its dynamics experiences a deceleration.
The glass ends up on a different, probably densified, amorphous configuration in which the ring size distribution changes towards smaller values. The accumulation of radiolytic events makes the glass to undergo a solid-to-solid transition via a non-thermal annealing, possibly corresponding to a different position in the Potential Energy Landscape (PEL) [2] or even to a landscape modification.

References

Hobbs, L. W. & Pascucci, M. R. *Journal de physique colloques*, **41**, C6-237. (1980)

Gupta, P. K . & Kob, W. *J. Non-Cryst. Sol. X*, **3**, 100031. (2019)(DOI: 10.1016/j.nocx.2019.100031)

Primary author(s) : ALFINELLI, Erica (Department of Physics, University of Trento (IT)); Dr. MARTINELLI, Alessandro (4Physics and Astronomy Department, University of Padova,); Dr. DALLARI, Francesco (Hasylab at DESY); ZANATTA, Marco; Prof. BALDI, Giacomo (Physics Department, University of Trento)

NEUTRONS FOR SOCIETY
ESRF
ADD2022
Analysis of Diffraction Data in Real Space
16-21 Oct 2022
Grenoble, France

Abstract ID : **69**

Thursday 20 Oct, 13:55

Using 3D-ΔPDFs from electron diffraction data to determine local structure

Ella Schmidt

Many functional materials have surprisingly simple average structures, but often partially occupied sites indicate disorder. To understand structure property relationships in complex ordered materials a description including local order is needed. Powder pair distribution functions are often used to quantitatively analyse the local structure of a material but the determination of three-dimensional local order principles requires complex modelling. For single crystal diffuse scattering data, the recently established three-dimensional delta pair distribution function (3D-ΔPDF) is the perfect tool to map local deviations from the average structure and provides a straightforward interpretation of local ordering principles [1].
To obtain 3D-ΔPDFs single crystals are needed which are suitable for the measurement with X-rays (approx. $(50\ \mu\text{m})^3$) or neutrons (approx. $(0.5\ \text{mm})^3$). Samples of these sizes are often hard to obtain for novel functional materials. Here, we demonstrate how the 3D-ΔPDF can be obtained from electron diffraction data which can be used on samples as small as $(10\ \text{nm})^3$.
For our proof of principle study, we use the high temperature ion conductor yttrium stabilized zirconia $Zr_{0.82}Y_{0.18}O_{1.91}$ (YSZ). YSZ crystallizes in the fluorite structure and shows composition disorder on both the metal and oxygen site. The substitution of Y^{3+} for Zr^{4+} on the metal site results in oxygen vacancies for charge compensation. Locally, O^{2-} ions relax towards the vacancies, while the metal-ions relax away from them.
Single crystals of YSZ were investigated with electron, X-ray and neutron diffraction. Highly structured diffuse scattering is observed alongside the sharp Bragg reflections. By comparing the results from our electron ΔPDF to X-ray and neutron ΔPDFs we demonstrate the reliability of the 3D-ΔePDF. A detailed analysis of the intensity distribution in the 3D-ΔPDF in the vicinity of the nearest neighbour inter-atomic vectors allows us to quantify the local structure relaxations.
To our knowledge, this is the first 3D-ΔePDF ever reported. This has important implications for the large variety of disordered materials of which single crystals for X-ray or neutron techniques are not available. In those cases, the 3D-ΔePDF will pave the way to understanding and tailoring physical properties that are determined by local structure variations.

Weber, T., & Simonov, A. (2012). Z. Kristallogr., 227(5), 238-247.

Primary author(s) : SCHMIDT, Ella Mara (University of Bremen)

Co-author(s) : Dr. KRYSIAK, Yasar (Institute of Inorganic Chemistry of the Leibniz University Hannover, Germany); Dr. KLAR, Paul Benjamin (Departement for Geosciences, University of Bremen); Dr. PALATINUS, Lukas (2Department of Structural Analysis, Institute of Physics of the CAS)

Abstract ID : **102**

Thursday 20 Oct, 14:40

Quantitative analysis of diffuse electron scattering in the lithium-ion battery cathode material Li1.2Ni0.13Mn0.54Co0.13O2

Romy Poppe

Materials with short-range order produce diffraction patterns that contain both Bragg reflections and diffuse scattering. Our study shows, for the first time, a refinement of short-range order parameters from the diffuse scattering in single-crystal electron diffraction data. The approach was demonstrated on the lithium-ion battery cathode material Li1.2Ni0.13Mn0.54Co0.13O2, for which the crystals are too small to be investigated with single-crystal X-ray or single-crystal neutron diffraction. Both the amount of stacking faults and the percentage of the different twins in the crystal were refined from the intensity distribution of the diffuse streaks using a differential evolutionary algorithm in DISCUS [1].

The approach was applied on reciprocal space sections reconstructed from three-dimensional electron diffraction (3D ED) data since they exhibited less dynamical effects compared to in-zone precession electron diffraction (PED) patterns. The effect of dynamical scattering and thermal diffuse scattering on the intensity distribution of the diffuse streaks will also be discussed.

Funding information
The research leading to these results has received funding from the Research Foundation Flanders (FWO Vlaanderen) (grant No. G035619N and grant No. G040116N).

[1] Proffen, T., & Neder, R. B. (1997). J. Appl. Crystallogr. 30, 171-175.

Primary author(s) : Ms. POPPE, Romy (University of Antwerp)

Co-author(s) : Mrs. VANDEMEULEBROUCKE, Daphne (University of Antwerp); Prof. NEDER, Reinhard (Friedrich-Alexander-Universität Erlangen-Nürnberg); Prof. HADERMANN, Joke (University of Antwerp)

Abstract ID : **104**

Thursday 20 Oct, 15:05

Diffuse scattering from phase-field-simulated ferroelectric textures

Petr Ondrejkovic

Over the last decade, an impressive progress has been made in exploration of ferroelectric domain structures from typical herringbone structures to nanoscale polar vortices and diverse flux-closure domain patterns [1,2]. Such studies are usually supported by phase-field simulations based on a generalized Ginzburg-Landau theory to explore local polarization and disentangle role of fundamental interactions [2,3]. One reliable way to validate simulated textures is to compare their neutron or X-ray diffuse scattering fingerprints with experimental data [4].
We will present calculation of diffuse scattering from selected ferroelectric domain structures obtained with phase-field simulations using the program Ferrodo [3], more concretely from herringbone structures consisting of 90-degree and 180-degree domain walls and from polar textures in ferroelectric-paraelectric superlattices. We will compare results with experimental data available in literature. Particularly, we will focus on performance of programs devoted to modelling of single crystal diffuse scattering, such as *Discus* [5] and the recently developed *MP_tools* [6].

Acknowledgement: This work was supported by the Czech Science Foundation (project No. 19-28594X).

\[1] J. Hlinka and P. Ondrejkovic, *Skyrmions in ferroelectric materials*, Chapter 4 in *Recent Advances in Topological Ferroics and their Dynamics*, edited by Robert L. Stamps, Helmut Schultheiß, in series Solid State Physics, Vol. 70, pp. 143–169, Academic Press (2019).
\[2] M. Hadjimichael, Y. Li, E. Zatterin *et al.*, *Nat. Mater.* **20**, 495 (2021).
\[3] P. Marton and J. Hlinka, *Phase Trans.* **79**, 467 (2006).
\[4] T. Yang, C. Dai, V.A. Stoica *et al.*, *Acta Materialia* **239**, 118258 (2022).
\[5] Th. Proffen and R.B. Neder, *J. Appl. Cryst.* **30**, 171 (1997).
\[6] J. Kulda, *Acta Cryst. A* (2022) in preparation, https://github.com/jkulda/MP_tools.

Primary author(s) : ONDREJKOVIC, Petr (Institute of Physics of the Czech Academy of Sciences); KULDA, Jiri (Institut Laue Langevin); PAŚCIAK, Marek (Institute of Physics of the Czech Academy of Sciences); MARTON, Pavel (Institute of Physics of the Czech Academy of Sciences); HLINKA, Jiri (Institute of Physics of the Czech Academy of Sciences)

Abstract ID : **120**

Thursday 20 Oct, 16:00

Randomness and frustration in a S = 1/2 square-lattice Heisenberg antiferromagnet

Ellen Fogh

We explore the interplay between randomness and magnetic frustration in the series of S = 1/2 Heisenberg square-lattice compounds $Sr_2CuTe_{1-x}W_xO_6$. Substituting W for Te alters the magnetic interactions dramatically, from strongly nearest-neighbor (J_1) to next-nearest-neighbor (J_2) antiferromagnetic coupling. We perform neutron scattering measurements to probe the magnetic ground state and excitations over a range of x and propose a bond-disorder model that reproduces ground states with only short-ranged spin correlations in the mixed compounds. The calculated neutron diffraction patterns and powder spectra agree well with the measured data and allow detailed predictions for future measurements. We conclude that quenched randomness plays the major role in defining the physics of $Sr_2CuTe_{1-x}W_xO_6$ with frustration being less significant.

Primary author(s) : FOGH, Ellen; MUSTONEN, Otto (Univeristy of Birmingham); BABKEVICH, Peter (École Polytechnique Fédérale de Lausanne); KATUKURI, Vamshi M. (Max Planck Institute for Solid State Research); WALKER, Helen (ISIS Neutron and Muon Source); MANGIN-THRO, Lucile (ILL); KARPPINEN, Maarit (Aalto University); WARD, Simon (ESS - DMSC); NORMAND, Bruce (Paul Scherrer Institute); RONNOW, Henrik

Abstract ID : **76**

Thursday 20 Oct, 16:45

Understanding synthesis-driven structure-property relationships in quantum materials

Jennifer Graham

Quantum materials are a broad class of systems that exhibit many unusual and exotic phenomena [1]. However, the complexity of these materials often leads to debates about how these exotic phenomena are manifested within them. One such material in which a consensus over the chemical and magnetic ground states are lacking is ZnV2O4. ZnV2O4 is an S = 1, cubic spinel which contains a geometrically frustrated pyrochlore sublattice. Previous studies have shown that the magnetic ground state for ZnV2O4 appears to be highly sample dependent, ranging from a conventional antiferromagnet to an unconventional and highly frustrated spin glass [2-7]. We hypothesise that local deviations from the average chemical structure, which arise during the sample preparation, are at the heart of this problem. To explore this, we have prepared two powder samples of ZnV2O4 using different synthetic routes, one via a conventional solid-state route and the other via a novel rapid microwave-assisted method [8]. In this talk we will explore how synthesis impacts the evolution of the chemical and magnetic ground states of ZnV2O4, using high-resolution powder neutron and synchrotron X-ray diffraction and magnetometry to reveal the average structural and magnetic behaviour, and, X-ray pair distribution function analysis and diffuse neutron scattering data to understand the local structure.

References

1. C. Broholm et al., Science 367 6475 (2020)
2. M. Reehuis et al. Eur. Phys. J. B 35, 311 – 316 (2003)
3. Y. Ueda et al., J. Phys. Soc. 66, 3 (1997)
4. S. -H. Lee et al. Phys. Rev. Lett. 93, 156407 (2004)
5. S. Ebbinghaus et al. J. Alloys Compd., 370, 75 (2004)
6. A. J. Browne and J. P. Attfield, Phys. Rev. B, 101, 024112 (2020)
7. M. Singa and R. Gupta, Physica B: Condens. Matter, 563, 101 (2019)
8. E. E Levin et al. Chem Mater. 31 18, 7151 – 7159 (2019)

Primary author(s) : GRAHAM, Jennifer (ILL); Dr. COOLEY, Joya (UCSB); Dr. CONFALONIERI, Giorgia (ESRF); SONGVILAY, Manila (Institut Néel); Dr. FORTES, Dominic (ISIS); WILDES, Andrew (Institut Laue Langevin); STEWART, John ross; Dr. CLARK, Lucy (University of Birmingham)

Abstract ID : **91**

Thursday 20 Oct, 17:10

Planar Defects and morphology of CdSe QDs by SAXS/WAXS Total Scattering: Wurtzite versus Zincblende structure

Nicola Dengo

CdSe quantum dots (QDs) have been extensively studied in the last three decades because of their finely size- and shape- tunable optical and electronic properties. Its colloidal synthesis reached an advanced level of control over size and morphology, and fine engineering of the surface structure. Despite this, the fine control over nanocrystal defectiveness and the fundamental investigation of the surface structure and faceting still remains a highly challenging task that lacks established analytical approaches. We previously tackled this problem by combining X-ray total scattering techniques in the wide- (WAXS) and small-angle regions (SAXS) and using the Debye scattering equation (DSE) based modeling approach[1] to achieve a detailed characterization of size, morphology, and planar defects in oleate-capped zincblende CdSe QDs[2]. This DSE-based combined SAXS/WAXS method is now extended to the atomic-to-nanometer scale characterization of wurtzite ODPA-capped CdSe QDs in the 2.3 to 5.6 nm size range. The The NCs morphology is described as hexagonal truncated bipyramids, exposing {001}, {100} and {011} facets. The relative extension of the different facets was found being both size- and fault- dependent. The same atomistic models were simultaneously employed to model the WAXS region, where the presence of planar defects was introduced using a layer-by-layer approach in the model construction. The analysis indicated a radically different behavior of the planar defect concentration with comparison to the cubic CdSe QDs and extended results will be presented. This work shows the potential of the proposed analytical approach to untangle complex and intertwined features of crystal structure defectiveness and particles' morphology, which might have an important impact on the final properties of CdSe and semiconductors QDs in general.

Financial support by Fondazione Cariplo, CubaGREEN Project 2020-4382 is acknowledged.

Cervellino et al, J. Appl. Crystallogr., 2015, 48, 2026

Moscheni et al, ACS Nano. 2018, 12, 12558

Primary author(s) : Dr. DENGO, Nicola (Dipartimento di Scienza e Alta Tecnologia and To.Sca.Lab, Università dell'Insubria,); Dr. BERTOLOTTI, Federica (Dipartimento di Scienza e Alta Tecnologia and To.Sca.Lab, Università dell'Insubria); Dr. MOSCHENI, Daniele (Dipartimento di Scienza e Alta Tecnologia and To.Sca.Lab, Università dell'Insubria); Dr. DIRIN, Dmitry N (Department of Chemistry and Applied Biosciences, ETH Zürich; Empa-Swiss Federal Laboratories for Materials Science and Technology); Prof. KOVALENKO, Maksym V (Department of Chemistry and Applied Biosciences, ETH Zürich; Empa-Swiss Federal Laboratories for Materials Science and Technology); Dr. CERVELLINO, Antonio (SLS, Laboratory for Synchrotron Radiation-Condensed Matter, Paul Scherrer Institut); Dr. PEDERSEN, Jan Skov (Department of Chemistry and Interdisciplinary Nanoscience Center (iNANO), Aarhus University); Prof. MASCIOCCHI, Norberto (Dipartimento di Scienza e Alta Tecnologia and To.Sca.Lab, Università dell'Insubria); Dr. GUAGLIARDI, Antonietta (Istituto di Cristallografia and To.Sca.Lab, Consiglio Nazionale delle Ricerche)

Abstract ID : **61**

Friday 21 Oct, 8:55

Recent advancements in laboratory PDF data quality

Mirijam Zobel

Although the very first laboratory-based X-ray pair distribution function (PDF) analysis had been carried out in the 1930s [1], laboratory PDF studies have been pretty uncommon till a few years back. [2] Limited momentum transfer vector Qmax, insufficient instrumental resolution and very long measurement times impeded a routine use for structural refinements. A few years ago, we have significantly pushed instrumental resolution of PDF data in the laboratory by reducing air scattering and optimizing beamstop positioning for a diffractometer in transmission geometry, using a MYTHEN2 4K module to cover a large angular range. [3] The use of monochromatic Ag Kα1 radiation permitted laboratory PDF data to be fitted over interatomic distance ranges of several dozens of Angstroms, e.g. to refine PDF data of 7 nm TiO2 nanoparticles with a goodness-of-fit Rw as low as 0.222 over 70 Å. Since then and as very specialized PDF setups are not available in many laboratories, more diverse attempts to optimize laboratory PDF analysis have been carried out. Diffractometers using Goebel mirrors provide Kα1,2 mixtures, which results in overlap of PDF peaks beyond about 20 Å. However, recent advanced data processing evolved and, for instance, TOPAS can nowadays deconvolute the instrumental contributions such as wavelength mixtures, emission profiles or axial divergence, yielding less instrumentally dampened PDF data [4] – in particular for crystalline materials. This approach is showcased and compared to monochromatically measured laboratory PDF data. To conclude, and in light of recent pushes in high-energy X-ray detectors such as the HyPix-Arc series (Rigaku) or Photon III (Bruker) combined with high-flux microfocus sources, single crystal diffractometers can accomplish very decent PDF data in only about two hours. This approach is based again on Kα2 stripping, necessary for data fitting beyond 30 Å, and highlighted for poorly crystalline powders and solutions of polynuclear lanthanide complexes. [5]

[1] B. E. Warren, N. S. Gingrich, Phys. Rev. (1934) 46 (368)

M. J. Nijenhuis, J. T. Gateshki, M. Fransen, Z. Kristallogr. Suppl. (2009) 163

S.L.J. Thomä, et al., Rev. Sci. Instr. (2019) 90 (4), 043905-1 - 043905-5

A. A. Coelho, P. A. Chater, M. J. Evans, J. Appl. Cryst. (2021) 54, 444-453

D. Tsymbarenko, D. Grebenyuk, M. Burlakova, M. Zobel, J. Appl. Cryst. (2022), 55

Primary author(s) : ZOBEL, Mirijam

Abstract ID : **80**

Friday 21 Oct, 9:40

In situ diffraction and PDF studies on the structure and crystallization of perovskite based catalysts for oxygen evolution reaction

Haritha Cheraparambil

Electrochemical water splitting is an effective way to store intermediate electricity from renewable energy sources. Water electrolyzers generate hydrogen at the cathode (hydrogen evolution reaction, HER) while oxygen forms at the anode (oxygen evolution reaction, OER). OER involves a complex four electrons transfer and is therefore considered the bottleneck of the water splitting reaction.\[1\] To date, iridium- and ruthenium-based materials are among the best-performing OER catalysts in alkaline conditions.\[2\] However, the scarcity and high cost of these precious metals have encouraged tremendous research in efficient and low-cost alternatives for OER catalysts, among which perovskites have demonstrated excellent OER activities because of their tunable chemical and electronic properties and their stability under different reaction conditions. \[3\]

The conventional synthetic routes for phase pure perovskites need high calcination temperatures and they result in large crystallites and low active surface area. However, phase purity and accessible active surface area play a critical role in electro-catalytic performance. Our work is directed towards the low-temperature synthesis and investigation of the structure-property relationship of highly active lanthanum-based perovskites for alkaline OER. The synthesis route via solution combustion of nitrate precursor solutions in the presence of a fuel followed by calcination is optimized. As obtained perovskites show high catalytic performance for OER. In order to have a comprehensive understanding of the structure-property relationships of these catalysts, the crystallization pathway has been studied via in situ diffraction and total scattering experiments.

The synthesis leads first to the formation of spongy precursors, which are amorphous, and the solid-state reaction from the amorphous phase to the crystalline perovskite is quite fast as observed in the in situ x-ray diffraction data. To gather more information on the local atomic scale but also intermediate- and long-ranges, we performed temperature dependent total scattering experiments and subsequent pair distribution function (PDF) analysis. From the PDF refinements, we observe that the so-obtained spongy precursor after a dynamic self-combustion is a combination of distorted oxides and meta-stable higher-order perovskites. With the temperature increase, we could follow the decomposition of meta-stable phases to corresponding oxides and Ruddlesden Popper phases. Around 550℃ we observe the formation of crystalline perovskite. Rietveld analysis and Fourier difference analysis reveal a deviation from the perfect crystal structure. The disorders are further studied by transmission electron microscopy, which confirms the presence of stacking faults. The combined effect of enhanced surface area, phase purity, and stacking faults are further correlated to the excellent OER performance of the catalysts.

Primary author(s) : CHERAPARAMBIL, Haritha (Max-Planck-Institut für Kohlenforschung)

Co-author(s) : Dr. PETERSEN, Hilke (Max Planck Institüt für Kohlenforschung); Dr. WEIDENTHALER, Claudia (Max planck Institüt für Kohlenforschung)

NEUTRONS FOR SOCIETY
ESRF
ADD2022
ANALYSIS OF DIFFRACTION DATA IN REAL SPACE
16-21 OCT 2022
GRENOBLE, FRANCE

Abstract ID : **73**

Friday 21 Oct, 10:05

Imaging Buried Dislocations in Halide Perovskites with 3D Strain Mapping

Kieran Orr

Halide perovskite have garnered significant attention as materials for use in solar cell and lighting applications, and over the last decade, device efficiencies of halide-perovskite based solar cells have risen from 14.1% (2013)[1] to 25.7% (2022)[2]. However, much of this improvement has been the result of empirical optimisation of fabrication procedures and our understanding of the light absorbing halide perovskite materials lags behind. It has become evident that strain plays an important role in determining device efficiency and long-term stability,[3] but the precise mechanism by which strain affects the materials' optoelectronic properties remains unclear.

In this talk, I will present our recent work investigating the internal structure of the archetypical $MAPbBr_3$ halide perovskite ($MA = CH_3NH_3$) using Bragg coherent diffraction imaging measurements[4] carried out at the Diamond Light Source, UK. This technique allows us to view the atomic displacement fields within our $MAPbBr_3$ material in the form of real space crystal reconstructions. By analysing these displacement fields, we are able to identify ⟨110⟩ and ⟨100⟩ edge dislocations in $MAPbBr_3$, the latter for the first time. Further, by using in situ measurements we also uncover that these dislocations become significantly more mobile under illumination with visible light. Solar cells (obviously) must be illuminated during operation, therefore, this light-induced dislocation migration gives us an insight into the buried nanoscale changes occurring in halide perovskite materials during device operation. Further, we intentionally study a subset of crystals that degrade under exposure to the X-ray beam, and by combining the coherent diffraction imaging data with photoluminescence microscopy, we discover that dislocation formation is a key step in material (and therefore device) degradation.

Our results provide unique insight into the nanoscale structure of halide perovskite materials, and show how the internal strain state of the materials evolves with time under operational stressors, and is therefore of significant interest to the halide perovskite, and materials science fields.

[1] Burschka, J. et al. Sequential deposition as a route to high-performance perovskite-sensitized solar cells. Nature, **499**, 316–319 (2013).

Best Research-Cell Efficiency Chart. https://www.nrel.gov/pv/cell-efficiency.html.

Liu, D. et al. Strain analysis and engineering in halide perovskite photovoltaics. Nat. Mater., **20**, 1337–1346 (2021).

Miao, J. et al. Beyond crystallography: Diffractive imaging using coherent x-ray light sources. Science, **348**, 530–535 (2015).

Primary author(s) : ORR, Kieran (University of Cambridge)

Co-author(s) : Prof. STRANKS, Samuel (University of Cambridge)

Abstract ID : **142**

Friday 21 Oct, 11:00

Structural and magnetic disorder in defect spin ice $Ho_2Ti_{1.5}Sc_{0.5}O_{6.75}$

Tomás Northam de la Fuente

Geometrically frustrated systems have been a topic of discussion for a number of years with particular interest in quantum spin liquids, states of quantum magnets in which electronic spins reside in macroscopic superpositions of infinitely many microstates, and spin-ice, with an important example being the pyrochlore $Ho_2Ti_2O_7$ [1]. The Ho ions of this sample are arranged in corner-sharing tetrahedra with an O ion, commonly labelled as O(1), in the centre of the tetrahedra, and every pair of Ho ions having a nearest neighbour O, commonly labelled as O(2), outside of the tetrahedra. The ground state configuration of this material is with two spins pointing in (towards the O) and two out (away from the O) of the tetrahedra. This two-in-two-out configuration is obeyed over a very long range at low temperatures, resulting in the appearance of bow tie like structures in reciprocal space called pinch points. As the temperature is increased, these pinch points broaden due to the emergence of magnetic monopoles [2], tetrahedra violating the two-in-two-out rule. Recently it has been predicted that for spin-ice materials with non-Kramers ions, such as $Ho_2Ti_2O_7$, it is possible to tune between classical and quantum spin liquid behaviour with long-range entanglement via the controlled introduction of structural disorder [3].

Measurements on highly defective single-crystal $Ho_2Ti_{1.5}Sc_{0.5}O_{6.75}$ at a temperature of 50 mK were performed using the diffractometer D7 at the Institut Laue-Langevin. The capability of this instrument to use polarized neutrons was used to properly separate the magnetic and nuclear contributions. Density functional theory calculations were performed and compared with the nuclear diffuse scattering data. We find that the oxygen vacancies are on the O(2) sites next to pairs of rare-earth ions. Crystal electric field measurements and point charge model calculations show that for this structural defect the nearest neighbouring Ho ions have non-magnetic singlet ground states [4]. The magnetic diffuse scattering data showed well-defined pinch points in agreement with Monte Carlo modelling and as predicted for the removal of spins from spin ice [5].

[1] T Fennell et al., Science 326 (2009) 415-17.

C Castelnovo et al., Nature 451 (2008) 42–45.

L. Savary et al., Phys. Rev. Lett. 118 (2017).

G. Sala et al. Nat. Mater 13 (2014) 488–493.

A Sen et al., Phys. Rev. Lett. 114 (2015).

Primary author(s) : NORTHAM DE LA FUENTE, Tomas

Co-author(s) : GOFF, Jon (Royal Holloway University of London); MANGIN-THRO, Lucile (ILL)

Abstract ID : **67**

Friday 21 Oct, 11:45

The short-ranged order in the van der Waals spin glass $Mn_{0.5}Fe_{0.5}PS_3$

Andrew Wildes

$MnPS_3$ and $FePS_3$ are both layered, van der Waals compounds that adopt long-ranged antiferromagnetic order below their relatively high Néel temperatures of 78 K and 120 K respectively. $Mn_{0.5}Fe_{0.5}PS_3$, however, is magnetically frustrated and instead is a spin glass with a freezing temperature of 35 K. The frustration is due to a competition between the nearest-neighbour magnetic exchanges, which are antiferromagnetic in $MnPS_3$ and ferromagnetic in $FePS_3$. We have studied the neutron diffuse scattering from both powdered and single crystal $Mn_{0.5}Fe_{0.5}PS_3$, using the D7 diffractometer with polarization analysis to separate the different contributions. The data were analysed using Reverse Monte-Carlo methods to determine the atomic structure and spin-spin correlations. The results from our analysis with be presented and described using a model based on a comparison of the ordered magnetic structures of the two parent compounds. We are further able to study the temperature-dependence of the magnetic correlations to determine the nature of the moment-freezing on entering the spin glass state.

Primary author(s) : Ms. GRAHAM, Jennifer (Institut Laue-Langevin); Dr. COAK, Matthew (University College London); Dr. SON, Suhan (Seoul National University); SUARD, Emmanuelle; Prof. PARK, Je-Geun (Seoul National University); Dr. CLARK, Lucy (University of Birmingham); WILDES, Andrew (Institut Laue Langevin)

Abstract ID : **90**

Friday 21 Oct, 12:10

Tuning local structure in Prussian blue analogues (PBAs)

Yevheniia Kholina

Prussian Blue analogues, M[M'$(CN)_6$]$_{1-x}$ n·H_2O, which we abbreviate here as M[M'] (M and M'=transition metal ions), is a diverse family of cyanide materials, which is intensely investigated for its potential application for hydrogen storage, as catalysts and as electrode materials. Applications that require efficient mass transport utilize the ability of the structure to accommodate a large number of M'$(CN)_6$ vacancies, which create a highly connected porous network. It was theoretically shown that the connectivity and the accessible volume of such a network depend on the local structure[1]. Therefore, to optimize mass transport properties not only the number of vacancies but also their distribution must be precisely controlled. In this work we show how to tune the local structure of Mn[Co] Prussian Blue analogues grown in gel by varying the crystallization parameters: the type of gel, the crystallization temperature, the concentration of reactants, and the concentration of chelating agents. We probe the defect distribution by single-crystal x-ray diffuse scattering, which allows quantitative characterization of the local structure. All of the above-mentioned parameters allow smooth continuous control of diffuse scattering and thus of the local order in Mn[Co] crystals.

[1] A. Simonov, et. al., Nature 578.7794, 256-260 (2020).

Primary author(s) : KHOLINA, Yevheniia; SIMONOV, Arkadiy

Abstract ID : **114**

Friday 21 Oct, 14:00

EIGER2 Upgrade: New Features for Advanced X-Ray Diffraction Experiments

Max Burian

Hybrid photon counting (HPC) X-ray detectors are crucial components for cutting-edge synchrotron research [1] by providing noise-free detection with advanced acquisition modes. In this regard, the latest HPC detector generation EIGER2 is setting new performance standards that push current horizons in X-ray science. These detectors combine all advantages of previous HPC detector generations while offering (i) 75 µm × 75 µm pixel size, (ii) kilohertz frame rates, (iii) negligible dead time (100 ns), and (iv) count rates of more than 107 photons per pixel.

Here, we evidence how the recently announced feature upgrade extends the capabilities of the EIGER2 and enables faster and cleaner crystallography experiments. We present how the detector enables powder diffraction experiments at up to 100 kHz, capturing transitions in-situ with <100 microsecond time resolution. Further, we show how to make use of the EIGER2s' two energy thresholds to reduce unwanted scattering contributions from higher-harmonics radiation, leading to cleaner and more unambiguous diffraction data. Supported by experimental data from multiple beamlines around the world, these results evidence how the new EIGER2 acquisition features will advance X-ray diffraction experiments for both static and time-resolved crystallography.

[1] Förster, A., et al. (2019) Philos. Trans. R. Soc. Math. Phys. Eng. Sci. 377, 20180241.

Primary author(s) : Dr. BURIAN, Max (DECTRIS Ltd.)

Co-author(s) : Mr. BRANDSTETTER, Stefan (DECTRIS Ltd.)

NEUTRONS FOR SOCIETY

ESRF

ADD2022

ANALYSIS OF DIFFRACTION DATA IN REAL SPACE

16-21 OCT 2022

GRENOBLE, FRANCE

Posters

Wednesday 19 Oct
18:00 - 21:00

Abstract ID : **63**

Bridging manganese clusters and materials formation: Polymorphism control in manganese oxide nanoparticles in hydrothermal synthesis

Nicolas Magnard

Manganese oxides can adopt several stoichiometries thanks to the relative stability of the Mn ion in oxidation states +2, +3 and +4, and accommodate cations of different sizes, leading to a range of different layered and tunneled crystal structures. [1, 2] On top of that, structural defects such as De Wolff disorder and micro-twinning can lead to the formation of defect-driven phases such as γ-MnO2 [3] which is an intergrowth of pyrolusite β-MnO2 and ramsdellite R-MnO2. Each of these phases have distinct properties, and synthetic control of polymorph formation is crucial. Here, we use in situ X-ray total scattering and PDF analysis supported by in situ XANES to study the formation mechanism leading to different manganese oxide polymorphs during hydrothermal synthesis. PDF analysis allows to follow structural changes all the way from the precursors in solution to the final product. We show that by changing the ratio between manganese(II) salt and oxidizer, it is possible to not only select between R, β- and α-MnO2, but more importantly the formation mechanism differs as well. Furthermore, we show that this processes involve intermediate manganese oxido-clusters, structurally similar to those found in nature or in molecular magnets,[4, 5] which act as building blocks in the formation of the crystalline nanoparticles.

1. Fortunato, J., et al., Surveying manganese oxides as electrode materials for harnessing salinity gradient energy. 2020. 54(9): p. 5746-5754.
2. Robinson, D.M., et al., Photochemical water oxidation by crystalline polymorphs of manganese oxides: structural requirements for catalysis. J Am Chem Soc, 2013. 135(9): p. 3494-501.
3. Hill, L.I. and A. Verbaere, On the structural defects in synthetic γ-MnO2s. Journal of Solid State Chemistry, 2004. 177(12): p. 4706-4723.
4. Yano, J. and V.J.C.r. Yachandra, Mn4Ca cluster in photosynthesis: where and how water is oxidized to dioxygen. 2014. 114(8): p. 4175-4205.
5. Charalambous, M., et al., [Mn14] "Structural Analogues" of Well-Known [Mn12] Single-Molecule Magnets. 2018. 2018(35): p. 3905-3912.

Primary author(s) : MAGNARD, Nicolas

Co-author(s) : AALLING-FREDERIKSEN, Olivia; Dr. JUELSHOLT, Mikkel (University of Oxford); KIRSCH, Andrea; Mr. NIELSEN, Tobias Mølgaard (University of Copenhagen); Mrs. WANG, Baiyu (University of Copenhagen); JENSEN, Kirsten Marie (University of Copenhagen)

NEUTRONS FOR SOCIETY
ESRF
ADD2022
ANALYSIS OF DIFFRACTION DATA IN REAL SPACE
16-21 OCT 2022
GRENOBLE, FRANCE

Abstract ID : **65**

Diffused Magnetic Scattering on Disordered Crystalline Material Na2Mn3O7

Bikash Chandra Sha

Two dimensional (2D) geometrically frustrated magnetic systems are of current interest due to their rich properties. In this regard, the layered compound Na2Mn3O7 having novel 2D maple leaf lattice (MLL) of Mn4+ is of present interest. The crystal structure derived from neutron diffraction data reveal Na2Mn3O7 is composed of alternating layers of Mn3O72- slabs and Na-ions layers. The Mn3O72- layers are built with the edge-sharing MnO6 octahedra and are well separated by an intermediate Na-ion layer. The measured patterns contain both sharp and broad Bragg peaks. The broad peaks in the neutron diffraction patterns appear due to stacking faults of the Mn3O72- layers in the crystal structure of Na2Mn3O7. Low temperature neutron diffraction measurements reveal diffuse magnetic neutron scatterings, due to short-range magnetic ordering, have been found below ~100 K without any signature of long-range magnetic ordering down to 1.7 K. Dc magnetization study also reveal a broad peak around ~100 K indicating the short-range magnetic ordering.

In order to have the microscopic understanding on the crystal structure of the disordered material Na2Mn3O7 and consequently to understand the stacking faults quantitatively, the “RMCProfile”, software packages will be employed. Furthermore, to determine the spin-spin correlations from the diffused magnetic scattering data, “Spinvert” software will be employed. The School and Conference on Analysis of Diffraction Data in Real Space (ADD2022) will provide hands-on tutorials for training with various data-modelling software packages: DiffPy-CMI, diffpy.mpdf, DISCUS, Dissolve, EPSR, PDFgui, RMCProfile, Spinvert and Yell. The software packages, “RMCProfile” and “Spinvert” are directly related to my PhD work and will be very useful for my research work. Additionally, I will have the chance to interact with experts and other fellow participants from across the world who are working in the forefront field by attending ADD2022.

Primary author(s) : Mr. SAHA, BIKASH CHANDRA (Bhabha Atomic Research Centre); Dr. BERA, Anup Kumar (Bhabha Atomic Research Centre); Dr. YUSUF, Seikh Mohammad (Bhabha Atomic Research Centre)

Abstract ID : **66**

Anti-site disorder driven enhanced intrinsic anomalous Hall conductivity in spin gapless semiconducting Mn2CoAl Heusler compound

Nisha Shahi

Spin gapless semiconductors, a novel state of the material, have attracted immense interest in the field of spintronics because of the finite gap in one spin channel and no gap in another. This state has been experimentally investigated in the Mn2CoAl Heusler compound for the first time. The transport measurement reflects that this compound has larger anomalous Hall conductivity (AHC) compared to the theoretically reported value. The detailed structural analysis reveals that the system crystallizes with anti-site disorder between Mn and Al atoms. The scaling analysis of anomalous Hall data shows that the AHC is primarily governed by Berry curvature in momentum space. After considering the disorder in the theoretical calculation, the calculated intrinsic AHC due to momentum space Berry curvature is in good agreement with the experimental intrinsic AHC. The disorder affects the electronic band structure, which modulates the associated momentum space Berry curvature and further enhances the intrinsic AHC.

Primary author(s) : Ms. SHAHI, Nisha (School of Material Science and Technology, IIT-BHU, Varanasi, 221005)

5)

NEUTRONS FOR SOCIETY
ESRF
ADD2022
ANALYSIS OF DIFFRACTION DATA IN REAL SPACE
16-21 OCT 2022
GRENOBLE, FRANCE

Abstract ID : **68**

Tuning the Magnetization of Manganese (II) Carbonate by Intracrystalline Amino Acids

Arad Lang

The creation of inter-crystalline organic inclusions is one of Nature's strategies to enhance the mechanical properties of biominerals. As was shown synthetically for calcite, the most abundant marine biomineral, incorporated pinned organic species act as barriers for cracks and dislocations movement. Thus, they increase the hardness of the single-crystalline calcite host. Inspired by this phenomenon, we showed in the past that a variety of semiconductors, both fully inorganic and hybrid organic-inorganic, are able to incorporate single amino acids. This incorporation induces an increase in the optical band gap of the semiconducting host, which results from charge localization created by the incorporated amino acids.

Here, we decided to study the influence of amino acids incorporation on yet another set of properties, namely the magnetic properties of manganese (II) carbonate (MnCO3). Similarly to the isostructural calcite, we discovered that certain amino acids can be incorporated into the crystalline structure of the host. Using high-resolution powder X-ray diffraction (HR-PXRD, in ID22 of the ESRF), and by employing the Rietveld refinement method, we measured an anisotropic lattice expansion of both a- and c-parameters, resulting from amino acids incorporation. These lattice distortions can be relaxed upon heating and organics decomposition. When we measured the magnetic properties of amino acid-incorporated MnCO3, we observed the predicted paramagnetic behavior, namely, a positive and linear relation between the magnetization, M, and the applied magnetic field, H. Nevertheless, the magnetic susceptibility (which was taken as the slope of the M-H curve), was observed to decrease with the increase of incorporated amino acids concentration. This decrease follows the simple rule of mixtures, indicating the creation of a MnCO3-amino acid composite.

MnCO3 is known to possess a Néel temperature of about 32 K. At this temperature, it undergoes a magnetic phase transformation, from a paramagnetic to a canted antiferromagnetic phase, which exhibits a weak ferromagnetic behavior. When we repeated our M-H measurement at 2 K, we discovered an opposite trend: the increase in magnetic susceptibility upon the increasing amount of incorporated amino acid. Moreover, the Néel temperature itself decreases. We repeated our HR-PXRD measurements, this time at a temperature of 5 K. Here, Rietveld refinement revealed that during amino acids incorporation, the Mn-O inter-atomic distance inside the MnCO3 unit cell increases. This increase results in a weakening of the magnetic Dzyaloshinskii-Moriya interaction (DMI), which makes the MnCO3 crystal more magnetically compliant, and reduces the transformation temperature.

Finally, we performed neutron powder diffraction (NPD, both at 300 K and 3 K) to try and detect small changes in the structure of MnCO3, as it is known that neutrons are more sensitive to light elements (such as C and O). While similar lattice distortions were measured using NPD, a possible symmetry change was also detected. It seems that amino acids incorporation induces a deformation of the carbonate ions, which results is a reduction of the symmetry of the crystal from rhombohedral (*R-3c*, #167) to monoclinic (*C2/c*, #15). This change can also explain the change in the magnetic interactions in the crystalline host.

Primary author(s) : LANG, Arad (Technion - Israel Institute of Technology); Prof. POKROY, Boaz (Technion - Israel Institute of Technology)

Co-author(s) : Dr. POLISHCHUK, Iryna (Technion - Israel Institute of Technology); Dr. CONFALONIERI, Giorgia (ESRF); Dr. CATHERINE, Dejoie (ESRF); Dr. MANIV, Ariel (Physics Department, Nuclear Research Centre); POTASHNIKOV, Daniel (Technion/IAEC); Dr. CASPI, Elad (Physics Department, Nuclear Research Centre)

NEUTRONS FOR SOCIETY
ESRF
ADD2022
ANALYSIS OF DIFFRACTION DATA IN REAL SPACE
16-21 OCT 2022
GRENOBLE, FRANCE

Abstract ID : **70**

Investigation of O / N ordering in Perovskite-type Oxynitrides La1−xYxTa(O,N)3 on Long-range and Short Scale

Marc Widenmeyer

The band gap of perovskite-type oxynitrides are known to show a complex interrelation with the strain and the potential O/N ordering contrasting the behaviour of closely related oxides[1],[2]. Here, four selected materials with the nominal compositions (1) LaTaO2N, (2) LaTaON2, (3) La0.9Y0.1TaO2N, and (4) La0.9Y0.1TaON2 were investigated at 10 K and 300 K. First, for a determination of the long-range crystal structure via Rietveld refinements and secondly for a local crystal structure analysis by pair distribution function (PDF) analysis. Synchrotron diffraction data of La1−xYxTa(O,N)3 revealed that all samples crystallized in space group Imma[2]. Additionally, neutron diffraction was applied, since atomic form factors of O2− and N3− are almost equal in X-ray diffraction. Based on the symmetry discussion given by Porter et al.[3] five different O/N ordering models were set up. As a basis, the structure model in Imma with a statistical distribution of O and N was used. Four ordered models with cis- (Ima2 or I212121.) or trans-ordering (Imma and C2/m) of O and N in the Ta(O,N)6 octahedra are possible starting from Imma.[3] Among them, the determined structure models from XRD data (Imma with statistical distribution of O & N) were identified as the most suitable one. Further refinements based on these models including the occupation factors delivered a more complex picture. Starting from a microcrystalline precursor resulted in 2D-cis ordered oxynitrides (2) & (4), while the partial substitution of La3+ by Y3+ started to disturb the ordering. In contrast, starting from a nanocrystalline precursor led to a statistical distribution despite the different O:N ratios of oxynitrides (1) & (3)[4].
PDF analysis results at 10 K will be discussed exemplary based on (2) LaTaON2. First, the long-range disordered Imma structure model was tested in the range of 1.5 Å ≤ r ≤ 11 Å with particular focus on the region below 5.5 Å. This resulted in a high residual value and large Uiso values. The refinements of the site occupation factors or introduction of O/N ordering did not lead to a significant improvement of the G(r) fit. The longest axis of the N(2) ellipsoids were perpendicular to the Ta−N(2) bonds pointing to a tilting along the b-axis. Based on these findings, alternative tilting patterns were evaluated and Pnma (a−b+a−) was identified as most reasonable one. A significant deviation remains in the range ca. 2.2 Å ≤ r ≤ 3 Å representing the nearest La−O/N distances, which could point to a hidden order on local scale. Next, oxygen was placed in cis-order on the N(2) site resulting in alternating ...−N−N−N−... and ...−O−O−O−... rows running along the c-axis. This brought a clear improvement of the fit at low r and nearly equal Uiso values for N(1) and N(2) site representing a similar level of disorder for both anionic sites. However, this model did not provide any improvement at r ⊠ 6 Å suggesting that cis-ordering exists only at the local scale[4].
In summary, the local structure can be described as following: i) r ⊠ 6 Å a local cis-order of N and O is observed coupled to a a−b+a− (Pnma) tilting pattern, ii) up to ca. 11 Å the structure preserves the Pnma tilting pattern without N/O ordering, iii) for r > 11 Å Pnma nanodomains separated by anti-phase boundaries merge to the observed long-range structures in Imma.

References

[1] N. Vonrüti, et al., Phys. Rev. Mater. 2, 105401 (2018)

C. Bubeck et al., J. Mater. Chem. A 8, 11837 (2020)

S.H. Porter, et al., Cryst. Growth Des. 14, 117 (2014)

M. Widenmeyer et al., ILL experimental report 6-06-482 (2020)

Primary author(s) : Dr. WIDENMEYER, Marc (Technical University of Darmstadt); BUBECK, Cora (Technische Universität Darmstadt); Prof. SCAVINI, Marco (University of Milan); CUELLO, Gabriel Julio; Prof. WEI- DENKAFF, Anke (Technische Universität Darmstadt)

NEUTRONS FOR SOCIETY
ESRF
ADD2022
ANALYSIS OF DIFFRACTION DATA IN REAL SPACE
16-21 OCT 2022
GRENOBLE, FRANCE

Abstract ID : **72**

Structural characterization of molecular organic frameworks for heterogeneous catalysis

Isabella Kappel

Aiming at more sustainable chemical processes, the development of efficient catalysts plays a major role. In that context, the development of single-atom catalysts has a huge potential since they can bridge the gap between homogeneous and heterogeneous catalysis due to very good performance, better catalyst separation and handling as well as maximum metal utilization [1].

Single-atom catalysts based on carbon-nitrogen polymers with low metal loadings have shown applicability for several catalytic systems. For example, Ir-complexes bound to Covalent Triazine Frameworks show great activity and selectivity in the catalytic decomposition of formic acid [2], which is considered a potential hydrogen storage material. Interestingly, and contrary to common expectations a reductive treatment at elevated temperatures led to an increased catalytic performance. A transfer of this procedure to other supports and metals shall be analyzed. Graphitic carbon nitrides (g-CN) where 0.5wt. % Pd was immobilized is at the center of this research. A detailed local structure analysis shall give rise to structure-property relationships in such systems. However, the characterization comes with some challenges due to the amorphous nature of the catalysts. The evaluation of possibilities and limits of X-ray total scattering and subsequent pair distribution function (PDF) analysis to characterize the polymeric support material and the as-synthesized catalyst is aimed. By comparing calculated PDFs (DiffPy-CMI) based on periodic density functional theory (DFT) calculations of different g-CN models with varying interplanar distances and stacking sequences with experimental data it was found that the model which was calculated to be the most stable matched the experimental data best. Compared to the simulated PDFs the experimental PDF shows oscillations indicating packing of repeating entities. Furthermore, ex situ synchrotron X-ray total scattering measurements have been conducted, showing the importance of high energy radiation for a detailed structural analysis on the atomic scale.

[1] Soorholtz, Mario, et al. "Local platinum environments in a solid analogue of the molecular Periana catalyst." ACS Catalysis 6.4 (2016): 2332-2340.

Bavykina, A. V., et al. "Efficient production of hydrogen from formic acid using a Covalent Triazine Framework supported molecular catalyst." ChemSusChem 8.5 (2015): 809-812

Project funding by the cluster of excellence Fuel Science Center (FSC) and the cooperation with the working group of Prof. Regina Palkovits at the ITMC, RWTH Aachen University are gratefully acknowledged.

Primary author(s) : Mrs. KAPPEL, Isabella (Max-Planck-Institut für Kohlenforschung)

Co-author(s) : Mr. VENNEWALD, Maurice (RWTH Aachen University); Mrs. SACKERS, Nina (RWTH Aachen University); Mr. IEMHOFF, Andree (RWTH Aachen University); Dr. WEIDENTHALER, Claudia (Max-Planck-Institut für Kohlenforschung); Prof. PALKOVITS, Regina (RWTH Aachen University)

Abstract ID : **74**

Uncovering atomic structures by combining results from pair distribution function measurements with angular correlation measurements from scanning electron nanobeam diffraction patterns

Rebekka Klemmt

Many properties of materials are closely connected to their atomic structure. For example, a material can exhibit different properties depending on whether its atomic structure is crystalline or disordered [1]. To fully understand the connection between material properties and their atomic structure, it is crucial to determine the atomic structure precisely [2]. This is more challenging for disordered materials because they are more complex to describe than crystalline materials due to their lack of long range order [1]. Established to determine the short range order of disordered materials is the usage of the pair distribution function (PDF), which can be obtained from x-ray, electron or neutron diffraction patterns and describes the probability to find an atom in a distances r from a reference atom. However, a PDF can be obtained from varies different atomic structures, which differ in angular arrangements of the atoms. To unambiguously determine the structure of disordered materials additional measurements to PDF are necessary [3]. One method which can be used to determine local angular arrangements of atoms is the analysis of scanning electron nanobeam diffraction (SEND) patterns for angular correlations [4].
Various additional information to the averaged atomic distance determined from PDF can be obtained from angular correlation analysis of SEND pattern. It is possible to determine the contribution of different fold symmetries to each local diffraction pattern. This can be used for comparison of materials inter alia by determining average symmetry contributions, or by investigating the spatial distribution of a symmetry. Furthermore, it is possible to investigate curvature of an atom layer by following the azimuthal change of intensity peak positions [1].
To make this analysis method available for a larger community, it is important to understand the influence of measurement parameters, like for example sample thickness or data quality, as well as developing applicable methods to obtain the information from the measured SEND patterns. Our research starts at this point. By using different approaches we aim to establishing the angular correlation analysis of SEND patterns. For example, we are investigating the analysis results from activated carbon with different thicknesses, and we are working on finding good ways to discover hidden information's in noisy SEND patterns by using different pre-processing of the data.
By establishing the analysis of SEND patterns for angular correlations and combining the findings with the results of PDF measurements from x-ray diffraction data, we are contributing to the clarification of atomic structures of disordered materials.

[1] E. D. Bøjesen, T. C. Petersen, A. V. Martin, M. Weyland, A. C. Y. Liu, J. Phys. Mater. 3, 044002 (2020).

A. V. Martin, E. D. Bøjesen, T. C. Petersen, C. Hu, M. J. Biggs, M. Weyland, A. C. Y. Liu, Small, 2000828 (2020).

M. J. Cliffe, M. T. Dove, D. A. Drabold, A. L. Goodwin, PRL 104, 125501 (2010).

A. C. Y. Liu, M. J. Neish, G. Stokol, G. A. Buckley, L. A. Smilie, M. D. de Jonge, R. T. Ott, M. J. Kramer, L. Bourgeois, PRL 110, 205505 (2013).

Primary author(s) : KLEMMT, Rebekka (Interdisciplinary Nanoscience Center, Aarhus University); BØJESEN, Espen Drath (Interdisciplinary Nanoscience Center)

Abstract ID : **75**

Local structure of PdO/Al2O3 catalysts during reduction in liquid phase

Daniele Bonavia

Pd catalysts are widely used in catalysed hydrogenation reactions for the synthesis of fine and bulk chemicals, which are often conducted in liquid phase. Since the Pd active phase is commonly deposited in its oxidised form on the support (e.g. Al2O3), previous works sought to study how the catalyst activation procedure affects the reducibility of the PdO phase, as well as the properties of the supported Pd nanoparticles (dispersion, particle size, morphology, interaction with the support, structural order, and surface properties), and how these factors correlate with the catalyst behaviour in the hydrogenation reaction [1].
To build on previous knowledge on the effects of the nature of the pre-reducing agent on the reducibility of PdO/Al2O3 catalysts, we investigated the isothermal reduction of PdO supported on different polymorphs of Al2O3 in water in the presence of different reducing agents (NaBH4, HCOONa, gaseous H2), mimicking the synthetic procedure adopted in the industry.
At the ESRF beamline ID15A we used High-Energy X-Ray Diffraction (HE-XRD) and Pair Distribution Function Analysis (PDF) to quantify hydride, metallic, and oxide Pd phases in both reciprocal and real space. Our aim was to understand the kinetics of nucleation and consumption of the hydrides obtained during the in situ reduction, and investigate the structural changes in the Pd nanoparticles during both sections of the process.
We were able to observe the disappearance of the PdO phase upon reduction, the subsequent formation of metallic Pd and the nucleation of the Pd hydride phase at a time resolution of 1-2 s. Preliminary results reveal that different Al2O3 polymorphs influence the reduction process and that γ-Al2O3 is unable to support the formation of Pd hydrides under these experimental conditions. Rietveld refinements suggest that, as previously discussed by Kovaric et al. [2], the vast majority of the supports is a lower-simmetry, inter-grown composite phase and not a mixture of the ideal structures of the various polymorphs. Additionally, different reducing agents proved to require different concentrations in order to provide comparable results, suggesting a different extent of reducing ability.
The evolution of the hydrogenation and the subsequent oxidation upon reaction with a target substrate (p-chloronitrobenzene) was followed with the same high time resolution (1-2 s) by tracking the evolution of characteristic Pd and PdO features in XRD/PDF data. To attain a quantitative operando assessment, the whole experiment was also monitored with an online IR spectrometer to detect the presence and concentration changes of the reducing agents, substrate and product.

[1] Groppo E. et al., (2012), doi:10.1016/j.jcat.2011.11.018

L. Kovarik et al., J. Phys. Chem. C (2019), https://doi.org/10.1021/acs.jpcc.8b10135

Primary author(s) : Mr. BONAVIA, Daniele (ESRF)

Co-author(s) : Mr. RICCHEBUONO, Alberto (University of Turin); VOTTERO, Eleonora (Università di Torino); Dr. PELLEGRINI, Riccardo (Chimet S.p.A.); Dr. PIOVANO, Andrea (ILL); Dr. GROPPO, Elena (University of Turin); Dr. CHECCHIA, Stefano (ESRF); Dr. FERRI, Davide (Paul-Scherrer Institut)

Abstract ID : **77**

Surfactant-free microemulsions : how molecular dynamic reflects nano-structuration

Firoz Malayil Kalathil

Mixtures of simple molecules may lead to complex systems with unforeseen properties of particular interest such as reactivity or solubility. This is the case of aqueous solutions of alcohol and oil, typically found in all kind of liquors, cosmetics or solvents for liquid-liquid extraction.

The archetypical case of this family is the ternary mixture of water, ethanol and octanol. Its phase diagram presents a biphasic region with a critical point (Upper Solution Critical Temperature) close to which a strong nanostructuration of the liquid can be observed. In the biphasic region, this emulsion was termed Ouzo effect, following the greek beverage, commonly observed when the 40 % alcohol liquor is quickly diluted with water. In the monophasic state, a « pre-Ouzo » region has aslo been evidenced [1], extending between identified frontiers around the critical point (see Fig. 1, [2]). The structuration is also characterized by a structure factor presenting an Ornstein-Zernike behaviour, indicating the presence of aggregates of the order of 100 molecules similar to a micro-emulsion formed by a ternary water-poor mixture of octanol and ethanol and water, surrounded by a surface excess of ethanol that is immersed in a binary water-ethanol solution saturated with a low quantity of octanol.

In this system, we investigated, using QENS and various isotopic mixtures, the relaxation dynamic of each component along different composition lines crossing the phase diagram. The evolution of the diffusion coefficient is measured over a wave vector ranging from ~0.05 A-1 to 0.6 A-1, bridging the scale from characteristic droplet size to molecular distances, i.e. from collective to individual dynamics.

We will show how the dynamics also reflect the (nano)structural organisation.

Primary author(s) : Mr. MALAYIL KALATHIL, Firoz (PhD); PLAZANET, Marie (Laboratoire Interdisciplinaire de Physique); HOFFMANN, Ingo; PREVOST, Sylvain (Institut Laue-Langevin); ZEMB, thomas (cea icsm); ALBA-SIMIONESCO, Christiane

References [1] T. Zemb et al., PNAS (2016) 113, 4260–4265 [2] Sylvain Prévost, Sebastian Krickl, Stjepan Marčelja, Werner Kunz, Thomas Zemb, and Isabelle Grillo, Langmuir 2021 37 (13), 3817-3827

NEUTRONS FOR SOCIETY
ESRF
ADD2022
ANALYSIS OF DIFFRACTION DATA IN REAL SPACE
16-21 OCT 2022
GRENOBLE, FRANCE

Abstract ID : **78**

Understanding how green additives control crystallization at the nanoscale

Annet Baken

Additives - small amounts of (organic) molecules - are widely used to control crystallization processes. Examples include the creation of cement pastes with improved workability (approx. $20 billion/year are spent on cement additives), property control during synthesis of inorganic materials for catalysis or energy storage, and the prevention of scale formation during cleaning processes (e.g. laundry or dishwashing) and water treatment technologies. Increasing environmental awareness and new regulations, such as the ban of phosphonate-based formulations, are pushing the industry to develop more sustainable, i.e. biodegradable and/or biobased, additives. As many of the existing compounds were identified through empirical trial-and-error approaches, the rational development of efficient green crystallization modifiers requires fundamental understanding of their modus operandi at the nanoscale. We now aim to correlate the physicochemical properties of additive molecules with their functionality during the crystallization process and to pinpoint when and how these molecules are incorporated into the emerging crystalline framework. To achieve this, we are developing an in-situ time-resolved Pair Distribution Function (PDF) analysis combined with potentiometric titration routine to monitor the crystallization process from diluted solutions in the presence of different types of (green) additives. The first results on the portlandite system imply that different additives act differently on the nucleation process. In addition, we aim to elucidate the nucleation pathway of calcium carbonate by our experimental approach that allows probing the nanostructural evolution of very diluted systems.

Primary author(s) : BAKEN, Annet; VAN DRIESSCHE, Alexander; DI MICHIEL, Marco (ESRF); FERNANDEZ-MARTINEZ, Alejandro (ISTerre, CNRS & Univ. Grenoble Alpes); KELLERMEIER, Matthias

Abstract ID : **79**

In-situ synchrotron x-ray diffraction texture evolution study on the deformation mechanisms in nanocrystalline NiTi wires subjected to tensile testing at various temperatures

Xiaohui Bian

Tensile deformation of nanocrystalline NiTi wires at -90, 20, 90 and 150 ℃ until fracture was investigated by in-situ synchrotron x-ray diffraction texture analysis. Sequential 2D diffraction patterns were recorded continuously using fast 2D detector during the testing. In-situ texture evolution of parent austenite and product martensite phases was evaluated by simultaneous Rietveld refinement of the set of ~110 1D diffraction spectra obtained by segmentation (along azimuthal direction) and integration (along radial direction) of individual 2D patterns, and was presented using pole figures and inverse pole figures [1,2]. In NiTi alloy that undergoes martensitic transformation and/or deformation twinning during tensile test, the martensite texture evolves due to discontinuous lattice rotation, which is reflected as intensity variation of existing inverse poles or occurrence of new poles in the inverse pole figures. Besides textures, the sequential 1D diffraction spectra along the loading direction/wire axis were fitted to evaluate lattice plane responses (integrated intensity, lattice strain and peak width) of individual grain families in austenite and martensite diffracting along that direction.

In our recent work, we have determined deformation mechanisms in NiTi based on the results of post mortem TEM analysis of martensite variant microstructures and lattice defects in grains of the wire deformed up to various maximum strains [3]. The analysis of texture evolution in the present work is a complementary approach which provides statistically relevant experimental evidence (i.e., averaged information over the sample gauge volume) on the same - i.e. on deformation mechanisms activated in nanocrystalline NiTi wires subjected to various thermomechanical loads. The activity of various deformation mechanisms is evaluated based on simulation of texture evolution using an abstraction of "ideally fibre textured polycrystal", which establishes a link between the martensitic microstructure/texture and discontinuous lattice rotations (structure changes) due to martensitic transformation and all twinning modes in martensite, including irreversible deformation twins [4].

In contrast to the widely spread view that <011> type-II martensite twins dominate during stress induced martensitic transformation and martensite reorientation in NiTi single crystals and large grain size polycrystals, it is suggested that (001) compound twinning plays key role in nanocrystalline NiTi wires. Plastic deformation of oriented martensite in nanocrystalline NiTi wires proceeds via a combination of (20-1) and (100) deformation twinning and kinking assisted by 100 dislocation slip.
Determination of deformation mechanisms from texture evolution of austenite and martensite phases in conjunction with modelling framework capable of predicting lattice rotation changes is a novel concept and is extensible to any materials deforming via deformation mechanisms accompanied by discontinuous changes of crystal lattice orientation.

[1] Dreele, R. Quantitative texture analysis by Rietveld refinement. Journal of Applied Crystallography, 30 (1997) 517-525.

O'Donnell, J. et al. A scripting interface for GSAS-II. Journal of Applied Crystallography 51 (2018) 1244-1250.

Molnárová, O. et al. Evolution of martensitic microstructures in nanocrystalline NiTi wires deformed in tension. Acta Materialia 218 (2021) 117166.

Heller, L. et al. On the plastic deformation accompanying cyclic martensitic transformation in thermomechanically loaded NiTi. International Journal of Plasticity 111 (2018) 53-71.

Primary author(s) : BIAN, Xiaohui (Institute of Physics of the Czech Academy of Sciences); Dr. HELLER, Ludek (Institute of Physics of the Czech Academy of Science); Dr. TYC, Ondřej (Institute of Physics of the Czech Academy of Science); KADEŘÁVEK, Lukas (Institute of Physics of the Czech Academy of Science); Dr. ŠITTNER, Petr (Institute of Physics of the Czech Academy of Science)

NEUTRONS
FOR SOCIETY
ESRF
ADD2022
ANALYSIS OF DIFFRACTION DATA
IN REAL SPACE
16-21 OCT 2022
GRENOBLE, FRANCE

Abstract ID : **81**

Crystallization of ultra-small gold nanoparticles via non-crystalline pre-nucleation clusters

Raj Kumar Ramamoorthy

Ultra-small gold nanoparticles with distinct structures (icosahedra or decahedra [1]) exhibit unique physical properties that deviate from their bulk counterpart, making them equally interesting both from fundamental and application points of view. Despite their fundamental and application interests, various processes underlying the formation of ultra-small gold nanoparticles in solutions is not clear, which resulted in poor control in the final structure (size and morphology) of gold nanoparticles. Here, by using a wide range of X-ray techniques ranging from total X-ray scattering to small-angle X-ray scattering, in-situ synthesis of gold nanoparticles – by adding reducing agent: triisopropylsilane (TIPS) - in hexane solution was followed. Interestingly, the precursor solution before adding TIPS already contains non-crystalline pre-nucleation clusters (PNCs) with the mean size of about 4 nm. Upon adding the reducing agent, these PNCs made up of Au(III) transform to gold nanoparticles Au(0) with the mean size of about 2 nm via an intermediate state made up of Au(III)/Au(I). With these results, we show that gold nanoparticles investigated in this study don't follow classical nucleation theory instead they evolve via non-crystalline PNCs [2].

References

Jorge A. Vargas et al., ACS Nano, 2018, 12, 9521.

R. K. Ramamoorthy et al., Nanoscale, 2020, 12, 16173.

Primary author(s) : RAMAMOORTHY, Raj Kumar (INSA Toulouse)

Co-author(s) : Mrs. YILDIRIM, Ezgi (INSA Toulouse); Prof. VIAU, Guillaume (INSA Toulouse); RODRIGUEZ RUIZ, Isaac (Laboratoire de Génie Chimique de Toulouse, UMR 5503 CNRS-Université de Toulouse); Dr. VARGAS, Jorge A. (Unidad Académica de Física); Dr. LACROIX, Lise-Marie (INSA-Toulouse); Prof. TEYCHENE, Sebestien (INP Toulouse); Prof. PETKOV, Valeri (Central Michigan University); ROBLIN, pierre (laboratoire de génie chimique)

Abstract ID : **82**

Characterization of novel carbon xerogel materials for vanadium redox flow batteries

Priyanka Sharma

Carbon blacks are commercially used as conductive fillers in carbon – polymer composite bipolar plates (BPPs) for vanadium redox flow batteries (VRFBs). The degradation of such BPPs during overcharging is a known problem [1]. The type and structure of carbon black play important roles in electrode degradation under highly oxidizing overcharge conditions [2]. Unfortunately, it is impossible to customize the microstructure of carbon blacks. Therefore, there is a need for efficient carbons with tunable properties, which can replace carbon blacks. Carbon xerogels (carbogels) are potential candidates since they provide easy tailoring of porosity along with high electrical conductivity [3]. In this project, we explore the possibility of replacing the standard conductive filler with novel carbogels and, thereby, improving the electrochemical performance of VRFBs.
Here, we present a comparison between a commercial carbon black and as-synthesized carbogel. From microstructural analysis including total scattering and subsequent pair distribution function analysis, Raman spectroscopy and HR-TEM, we observe that carbon black contains slightly larger crystallites and is more ordered. However, the higher electrical conductivity of BPPs with carbon black as compared to its carbogel counterpart could be mainly attributed to the branched structure of carbon black particles. This study allowed us to focus on synthesis parameters of the carbogel, which influence the texture. As a result, BPPs with improved electrical conductivities have been produced. Further studies are ongoing.

References:

Parasuraman A, Lim TM, Menictas C, Skyllas-Kazacos M. Review of material research and development for vanadium redox flow battery applications. Electrochim. Acta, 101, 27-40 (2013)

Brungs A, Haddadi-Asl V, Skyllas-Kazacos M. Preparation and evaluation of electrocatalytic oxide coatings on conductive carbon-polymer composite substrates for use as dimensionally stable anodes. J. Appl. Electrochem., 26, 1117- 1123 (1996)

Rahman M. (ed.) Designing Nanostructured Carbon Xerogels. Nanomaterials. 2011, https://www.intechopen.com/chapters/25347, ISBN: 978-953-307-913-4

Primary author(s) : Mrs. SHARMA, Priyanka (Max-Planck-Institut für Kohlenforschung)

Co-author(s) : Dr. SCHMIDT, Wolfgang (Max-Planck-Institut für Kohlenforschung); Mr. BILICAN, Abdurrahman (Max-Planck-Institut für Kohlenforschung); Dr. WEIDENTHALER, Claudia (Max-Planck-Institut für Kohlenforschung)

NEUTRONS FOR SOCIETY
ESRF
ADD2022
ANALYSIS OF DIFFRACTION DATA IN REAL SPACE
16-21 OCT 2022
GRENOBLE, FRANCE

Abstract ID : **86**

Ionic Conductivity and Disorder in Sodium Perovskite Solid-State Electrolytes

Michael Brennan

The growing need for safe, reliable energy storage has brought the search for stable, high performance solid electrolytes to the forefront of battery material research. One approach to achieve these goals is to use the highly versatile perovskite structure. This structure, with the general formula ABX3, allows for a wide range of dopants which can be used to tailor the resulting ionic conductivities of perovskite solid electrolytes [1]. However, an overall mechanism remains elusive.

Recently, it has been shown that the ionic conduction of the sodium-based perovskite Na1/2¬La1/2-ZrO3 can be improved through the substitution of Sr2+ onto the A site, reaching a maximum ionic conductivity in Na1/2-xLa1/2-xSr2xZrO3 at x = 1/6. Zhao et al. propose that this increase in ionic conductivity is due to the widening of sodium conduction pathways caused by the addition of Sr2+ [2]. We have recently conducted experiments that showed doping the A site with larger Ba2+ cations further increased the ionic conductivity and sodium mobility, agreeing with the mechanism proposed by Zhao et al.

However, unlike the Sr2+ series, we have found that the ionic conductivity of the Ba2+ series reaches a local maximum at x = 1/6 but has a global maximum at x = 7/32, coinciding with disorder in the long-range structure as evidenced by X-ray diffraction. Disorder is well known to increase ionic conductivity in solid-state electrolytes. However, the nature of the disorder in this system, and the mechanism by which it increases ionic conductivity is not clear.

This poster will focus on upcoming total scattering experiments and pair distribution function analysis being performed at Institut Laue-Langevin (ILL). Quantification of the various coordination environments of the cations will allow for an investigation into the length scale of this disorder and how it evolves across the solid solution series. This will allow us to propose a mechanism to explain the increase in ionic conductivity of these materials.

1. Yan, S., et al., Perovskite Solid-State Electrolytes for Lithium Metal Batteries. Batteries-Basel, 2021. 7(4).
2. Zhao, Y.Z., et al., Synthesis and characterization of a new perovskite-type solid-state electrolyte of Na1/3La1/3Sr1/3ZrO3 for all-solid-state sodium-ion batteries. Journal of Alloys and Compounds, 2019. 783: p. 219-225.

Primary author(s) : Mr. BRENNAN, Michael (University of Sydney); Prof. LING, Chris (University of Sydney)

Abstract ID : **87**

Fast generation of diffuse scattering maps: MP_tools

Jiri Kulda

Modern materials often exhibit a considerable portion of structural disorder, playing a key role in their functionalities. In order to characterise local atomic arrangements and short-range correlations one has to investigate the shape of Bragg lines and the distribution of diffuse scattering below and between them.
To extract information from experimental data one has to compare model-based intensities with the observed ones. The progress in computing techniques in last decades permits to produce realistic models of crystalline lattices by a variety of approaches ranging from ab initio DFT methods via molecular dynamics (MD) to phase-field models based on the Landau formalism. Alternatively, one may retrieve the displacement pattern without making assumptions on its origin by reverse Monte-Carlo (RMC) modelling
With this progress in place the bottleneck has shifted from producing supercell models to generating the corresponding diffuse scattering distributions in reciprocal space. The principal issue being the fact that scattering amplitudes from a distorted lattice cannot be summed up using fast Fourier transform algorithms (FFT) because of the displacement phase factor exp(-i **QR**) being **Q**-dependent. As a consequence, many efforts in recent years have been restricted to simple models on small supercells [1,2] or to more involved pair distribution function (PDF) analysis [3-5], where the summation problem is reduced to a single dimension.
To address this issue, we will present a new approach [6], based on recent developments of the non-uniform fast Fourier transform (NUFFT) algorithm [7], implemented in the *MP_tools* program suite [8]. Diffracted intensity maps from model supercells containing millions of atoms as well as dynamic scattering functions S(**Q**,ω) based on time sequences of thousands of frames now can be calculated by several orders of magnitude faster in a truly interactive manner.

Many motivating discussions with my Prague colleagues Marek Pasciak, Petr Ondrejkovic and Jirka Hlinka from the Institute of Physics (AS CR) are kindly acknowledged.

[1] Welberry T.R., Butler B.: J. Appl. Cryst. 27 (1994) 205-231

Neder R.B., Proffen Th.: Diffuse Scattering and Defect Structure Simulations: A cook book using the program DISCUS, Oxford, 2008; DOI:10.1093/acprof:oso/9780199233694.001.0001

McGreevy R.L., J. Phys.: Condens. Matter 13 (2001) R877–R913

Proffen Th. et al., Z. Kristallogr. 218 (2003) 132–143

Eremenko M. et al., Nature Comm. 10 (2019) 2728

Kulda J., Acta Cryst. A (2022) in preparation

Barnett A.H. et al., J. Sci. Comput. 41 (2019) C479-C504, https://github.com/flatironinstitute/finufft

Kulda J., https://github.com/jkulda/MP_tools

Primary author(s) : KULDA, Jiri

Abstract ID : **88**

Nano Materials Analysis by Combination of PDF und (U)SAXS Recent Advances in Instrumentation from Malvern Panalytical.

Loïc Maze

X-ray powder diffraction is one of the most important techniques for material analysis with applications in areas ranging from pharmaceuticals to mining and from semiconductors to building materials. Each material presents its own challenges, and this creates a constant demand for improved data quality and shorter measurement times. Despite its long history, instrumentation for laboratory X-ray diffraction is in continuous development and recent years have marked significant progress in practically every component involved in the X-ray diffraction experiments.
The highly versatile Empyrean instrument enables a variety of X-ray scattering techniques for the structural and dimensional characterization of matter on multiple length scales. The Empyrean makes accessible on laboratory high-performance ultra-small-angle X-ray scattering (USAXS), small- and wide-angle X-ray scattering (SAXS/WAXS) as well as total scattering (atomic pair distribution function analysis; PDF) experiments. It covers Bragg spacings from sub-Angstroms to 1.7 microns, thus allowing the analysis of dimensions and complex structures in (nano-)materials on multiple length scales. The accessible scattering vector q-range spans over almost five decades (qmin = 0.0036 nm-1, qmax = 215 nm-1), without any gaps.
SAXS and USAXS allow to investigate the size distribution, internal structure, and shape of nanoparticles and macromolecules and to determine characteristic repeat distances in nanostructured materials. On the other hand, with the total scattering (PDF) technique, the local atomic structures in (partially) disordered materials can be studied. The combination of all scattering techniques thus enables the investigation of complex structures on the atomic and nano- and meso- (length) scales, which is essential for a better understanding of and control over the macroscopic properties of a given material.

Primary author(s) : MAZE, LOIC (Malvern Panalytical); GATESHKI, Milen (Malvern Panalytical); KOGAN, Vladimir A. (Malvern Panalytical); BECKERS, Detlef (Malvern Panalytical); BOLZE, Jörg (Malvern Panalytical)

Abstract ID : **89**

Multivariate Analysis of Synchrotron X-Ray data for Battery Research

Erlend Tiberg North

By utilizing multivariate analysis of x-ray operando data from working batteries one can separate and enhance scattering signals from specific components of the battery, identifying the critical responses that are connected to its performance and failure. This can enable faster and easier analysis of operando data, especially from complex materials that are difficult to analyze manually.

In this poster I will present the preliminary results that we have obtained so far, focusing mainly on comparing analysis methods on simulated data sets, along with the current plan of the research project in my PhD.

Primary author(s) : TIBERG NORTH, Erlend (University of Oslo)

Co-author(s) : WRAGG, David

NEUTRONS FOR SOCIETY
ESRF
ADD2022
ANALYSIS OF DIFFRACTION DATA IN REAL SPACE
16-21 OCT 2022
GRENOBLE, FRANCE

Abstract ID : **92**

Use of neutron and X-ray total scattering for improvement of nucleation modelling in engineering alloys

Monika Rolinska

Modelling of phase transformations is key in design of new materials. Accurate models on different length scales, ranging from atomistic modelling to finite element methods, help with design of materials with longer service lives and smaller environmental impact through the integrated computational materials engineering approach. Great advances have been made in recent decades, however, modelling of nucleation in solid-state phase transformations can still be improved. One of the challenges is the inherent difficulty of experimental studies of the nucleation event, linked to the small length-scale and short time during which it occurs. This difficulty has limited the input that could be used in modelling of early-stage phase transformations. It has been shown previously that the initial state on a short range is crucial for the phase transformation kinetics in duplex and ferritic stainless steels [1]–[4]. Total scattering and the associated pair distribution function analysis is one of the very few methods when the events leading up to nucleation, such as short-range interaction, can be studied. Use of total scattering opens up for the possibility to map the short-range order behaviour for different compositions and temperatures for systems such as iron-chromium (which is the basis for industrially important stainless steels), to be fed into models for more accurate predictions of the phase transformation kinetics and characteristics. This could ultimately lead to development of materials with improved properties.

References

J. Zhou, J. Odqvist, L. Höglund, M. Thuvander, T. Barkar, P. Hedström, Initial clustering - A key factor for phase separation kinetics in Fe-Cr-based alloys, Scr Mater. 75 (2014) 62–65. https://doi.org/10.1016/j.scriptamat.2013.11.020.

X. Xu, J.E. Westraadt, J. Odqvist, T.G.A. Youngs, S.M. King, P. Hedström, Effect of heat treatment above the miscibility gap on nanostructure formation due to spinodal decomposition in Fe-52.85 at.%Cr, Acta Mater. 145 (2018) 347–358. https://doi.org/10.1016/j.actamat.2017.12.008.

J. Zhou, J. Odqvist, A. Ruban, M. Thuvander, W. Xiong, J. Ågren, G.B. Olson, P. Hedström, Effect of solution treatment on spinodal decomposition during aging of an Fe-46.5 at.% Cr alloy, J Mater Sci. 52 (2017) 326–335. https://doi.org/10.1007/s10853-016-0333-6.

J. Liu, Y. Das, S.M. King, J.Y. Jonsson, S. Wessman, P. Hedström, Effect of Cooling Rate after Solution Treatment on Subsequent Phase Separation Evolution in Super Duplex Stainless Steel 25Cr-7Ni (wt.%), Metals 12 (2022). https://doi.org/10.3390/met12050890.

Primary author(s) : Ms. ROLINSKA, Monika (KTH Royal Institute of Technology)

Co-author(s) : Prof. ODQVIST, Joakim (KTH Royal Institute of Technology); Prof. HEDSTRÖM, Peter (KTH Royal Institute of Technology)

Abstract ID : **93**

Multiscale investigation of Gd2(Ti1-xZrx)2O7 pyrochlores matrices for radioactive waste disposal

Armando Di Biase

Crystalline A2B2O7 materials with the pyrochlore structure have drawn much attention for their potential usage in the field of radionuclides disposal. It has been demonstrated that pyrochlores belonging to Gd2(Ti1-xZrx)2O7 solid solution can withstand higher doses of ion irradiation without amorphizing as the Zr-content increases. The Zr-rich samples can effectively dissipate the irradiation energy by undergoing a phase transition from the pyrochlore to the defect fluorite structure. As a matter of fact, the pure cationic substitution of Ti4+ by Zr4+ in pristine Gd2(Ti1-xZrx)2O7 compositions drives progressive structural disordering.
The aim of this study was to investigate the structure of the Gd2(Ti1-xZrx)2O7 series at different length scales by means of diffraction and spectroscopic tools. All the samples are microcrystalline powders produced by solid-state reaction. The evolution of the average structure is assessed by Rietveld analysis of High-Resolution X-ray diffraction patterns. Substituting Ti with Zr in Gd2Ti2O7 compound, induces the progressive formation of Anti-Frenkel Oxygen defects and, for $x \geq 0.75$, slight cation A, B sites disordering (less than 5% in Gd2Zr2O7).
Insights into the local structure are given by Raman spectroscopy and Pair Distribution Function (PDF/G(r)) analysis. G(r) function of Gd2Ti2O7 is suitably fitted by the pyrochlore structure even at short r range ($r \leq 8$ Å) at difference with the Zr containing solid solutions and pure compound. Strong Fit improvement is obtained applying to Gd2Zr2O7 in the same range an approximated C2221 weberite model (with the same A2B2O7 composition): within it selected oxygen ions are moved to sites which are empty in the pyrochlore structure (anti-Frenkel defect formation) transforming the ZrO6 distorted octahedral cages into ZrO7 ones. Solid solutions are fitted in the same range by weighted linear combinations of pyrochlore and weberite models. For $r \geq 8$ Å the pyrochlore model suitably fits all the G(r) functions so reconciling the long-range picture with that at the local scale and suggesting that some Zr/Ti ordering should exist in solid solutions with sub-nanometer correlation length.
The sub-nanometer structural reconstruction, revealed by PDF analysis could be strictly related to Zr-rich solid solutions resilience to amorphization and should help designing efficient materials for long term nuclear waste trapping.

Primary author(s) : Dr. DI BIASE, Armando (Dipartimento di Chimica, Università degli Studi di Milano, via Golgi 19, 20131 Milano, Italy); Prof. CASTELLANO, Carlo (Dipartimento di Chimica, Università degli Studi di Milano, via Golgi 19, 20131 Milano, Italy); Dr. CONFALONIERI, Giorgia (ESRF - The European Synchrotron Radiation Facility CS 40220, Grenoble, Cedex 9 38043, France); Prof. FUMAGALLI, Patrizia (Dipartimento di Scienze della Terra, Università degli Studi di Milano, Via Botticelli 23, Milano 20133, Italy); Prof. TUMIATI, Simone (Dipartimento di Scienze della Terra, Università degli Studi di Milano, Via Botticelli 23, Milano 20133, Italy); Dr. CERESOLI, Davide (Istituto di Scienze e Tecnologie Chimiche "Giulio Natta" (SCITEC), Consiglio Nazionale delle Ricerche (CNR), PST via Fantoli 16/15, 20138 Milan and via Golgi 19, Milano 20133, Italy); Prof. SCAVINI, Marco (Dipartimento di Chimica, Università degli Studi di Milano, via Golgi 19, 20131 Milano, Italy)

Abstract ID : **95**

Dislocations depth distributions in GaN-on-Sapphire heteroepitaxial layers

Cosmin Romanitan

Wurtzite gallium nitride (wz-GaN) as one of the most promising wide bandgap semiconductor materials has limited applications in the modern optoelectronic devices. In the polar [0001]-oriented GaN, the dominant microstructural defects are threading dislocations (TDs), which are mainly generated in epitaxial layers due to the GaN/substate lattice mismatch [1-4]. The TDs act as harmful defects and play the role of charge scattering sites, non-radiative recombination centers, and leakage paths for current that severely degrades the efficiency of any GaN-based devices.

In this work, dislocations depth distributions in GaN-on-Sapphire (Al2O3) heteroepitaxial layers were investigated by using a non-destructive ultra-high resolution X-ray diffraction technique. A widely used standard X-ray diffraction methods (the mosaic block and diffuse scattering model, Williamson-Hall plot, X-ray reciprocal space maps (RSMs)) were employed for the analyses of the screw and edge TD density. Moreover, a new approach based on grazing incidence and glancing exit X-ray diffraction was developed. It allows us to analyse the TDs density along the GaN growth direction (c-axis) and correlate the data with the standard X-ray diffraction methods. A gradual decrease in TDs density towards the surface of GaN was revealed and discussed. Reliable non-destructive techniques for structural characterization of materials provide a better understanding of the materials growth, defect formation and opens new pathways for the efficient defect engineering and growth optimization.

1 - Kaganer, V. M., Brandt, O., Trampert, A. & Ploog, K. H. (2005). Phys. Rev. B - Condens. Matter Mater. Phys. 72, 1–12.
2 - Safriuk, N. V., Stanchu, G. V., Kuchuk, A. V., Kladko, V. P., Belyaev, A. E. & Machulin, V. F. (2013). Semicond. Phys. Quantum Electron. Optoelectron. 16, 265–272.
3 - Barchuk, M., Motylenko, M., Lukin, G., Patzold, O. & Rafaja, D. (2017). J. Appl. Crystallogr. 50, 555–560.
4 - Romanitan, C., Mihalache, I., Tutunaru, O. & Pachiu, C. (2021). J. Alloys Compd. 858, 157723.

Acknowledgments
The financial support was offered by the PN-III-P4-ID-PCE-2020-1712 project within PNCDI III, and Core Program PN 1916/2019 MICRO-NANO-SIS PLUS/08.02.2019.

Primary author(s) : Dr. ROMANITAN, Cosmin (National Institute for R&D in Microtechnologies)

Co-author(s) : Dr. VARASTEANU, Pericle (National Institute for R&D in Microtechnologies); Dr. WARE, Morgan E. (Institute for Nanoscience and Engineering, University of Arkansas, Fayetteville 72701, USA); Ms. BRINCOVEANU, Oana (National Institute for R&D in Microtechnologies); Dr. MAZUR, Yuriy I. (Institute for Nanoscience and Engineering, University of Arkansas, Fayetteville 72701, USA); Dr. KUCHUK, Andrian V. (Institute for Nanoscience and Engineering, University of Arkansas, Fayetteville 72701, USA)

NEUTRONS FOR SOCIETY
ESRF
ADD2022
ANALYSIS OF DIFFRACTION DATA IN REAL SPACE
16-21 OCT 2022
GRENOBLE, FRANCE

Abstract ID : **96**

Investigation of charge-induced structural disordering in NaCrO2 cathodes for Na-ion rechargeable batteries

Bettina Andersen

The scope of much energy related research today is to move towards more renewable energy sources. Existing components and materials within these sources should therefore be replaced with more green alternatives, e.g., iron, titanium, and sodium. The latter has, within battery research, also received a lot of attention in recent years due to the similarities to the well-established Li-ion battery technology, i.e. much know-how can be transferred to Na-ion batteries. Furthermore, sodium has a great abundance which is the main reason for the categorization of sodium to be a promising alternative to the Li-ion battery [1, 2].
However, when changing from lithium to sodium, challenges arise. One of these challenges is structural disordering being induced in some electrode materials during charge and/or discharge [3]. This is, among others, observed in layered sodium chromium oxide, NaCrO2. When Na-ions are extracted from NaCrO2 during battery charge the material is subjected to different structural transitions. When the Na-extraction exceeds a certain limit, the material suffers from severe capacity decay due to the formation of a highly disordered phase [4-6].

In this study, the disordering of NaCrO2 during Na-ion extraction has been investigated through total scattering and pair distribution function analysis. Additionally, the material has been studied through transmission electron microscopy and energy dispersive X-ray analysis to evaluate the particle size distribution and, moreover, the distribution of Na in the material.

1. Hwang, J.-Y., S.-T. Myung, and Y.-K. Sun, Sodium-ion batteries: present and future. Chemical Society Reviews, 2017. 46(12): p. 3529-3614.
2. Yabuuchi, N., et al., Research Development on Sodium-Ion Batteries. Chemical Reviews, 2014. 114(23): p. 11636-11682.
3. Christensen, C.K. and D.B. Ravnsbæk, Understanding disorder in oxide-based electrode materials for rechargeable batteries. Journal of Physics: Energy, 2021. 3(3): p. 031002.
4. Bo, S.-H., et al., Layered-to-Rock-Salt Transformation in Desodiated NaxCrO2 (x 0.4). Chemistry of Materials, 2016. 28(5): p. 1419-1429.
5. Yu, C.-Y., et al., NaCrO2 cathode for high-rate sodium-ion batteries. Energy & Environmental Science, 2015. 8(7): p. 2019-2026.
6. Kubota, K., et al., New Insight into Structural Evolution in Layered NaCrO2 during Electrochemical Sodium Extraction. The Journal of Physical Chemistry C, 2015. 119(1): p. 166-175.

Primary author(s) : Ms. ANDERSEN, Bettina Pilgaard; Mr. JAKOBSEN, Christian Lund; Dr. BØJESEN, Espen Drath; Prof. RAVNSBÆK, Dorthe Bomholdt

Abstract ID : **97**

Evaluation of halide perovskite precursor solutions using the reduced pair-distribution-function of mid-range SAXS data

Joachim Breternitz

One of the notable conceptual advantages of halide perovskite semiconductors for solar cells is the possibility to produce them based on solution processes at temperatures only slightly above room temperature [1]. Typically, the various precursors are dissolved in suitable solvents, such as γ-butyrolactone (GBL), dimethyl formamide (DMF) and dimethyl sulfoxide (DMSO) and these precursor solutions are evaporated to form halide perovskite films [2].

Those precursor solutions are not entirely homogeneous, but contain small agglomerations of perovskite building blocks [3]. The size of those building blocks depends both on the composition of the solvent as well as on the composition of the perovskite precursors, opening a huge parameter field to tune the precursor formulation with agglomeration sizes typically in the range of 1-5 nm. Small angle X-ray scattering (SAXS) is equipped to test this range, although those agglomeration sizes are at the lower end of the common probing size, i.e. with larger angle ranges than commonly measured. Our experiments at the ASAXS end station [4] operated at the PTB FCM beamline [5] at the BESSY II synchrotron, for instance, were performed in a momentum transfer range of 0.2 nm-1 ≤ q ≤ 8 nm-1. A larger reciprocal space resolution, on the other hand, allows for a better resolution in real space when performing a Fourier transformation to achieve a pair-distribution function (PDF). Herein, we assess a suitable approach for the reduced pair-distribution function for the analysis of our SAXS data and compare the results with simple peak analysis and model-based refinements.

References

F. Lehmann, A. Franz, D. M. Többens, S. Levcenco, T. Unold, A. Taubert, S. Schorr, *RSC Adv.* **2019**, *9*, 11151–11159.

S. Caicedo-Dávila, H. Funk, R. Lovrinčić, C. Müller, M. Sendner, O. Cojocaru-Mirédin, F. Lehmann, R. Gunder, A. Franz, S. Levcenco, A. V. Cohen, L. Kronik, B. Haas, C. T. Koch, D. Abou-Ras, *J. Phys. Chem. C* **2019**, *123*, 17666–17677.

M. A. Flatken, A. Hoell, R. Wendt, E. Härk, A. Dallmann, A. Prause, J. Pascual, E. Unger, A. Abate, *J. Mater. Chem. A* **2021**, *9*, 13477–13482.

A. Hoell, I. Zizak, H. Bieder, L. Mokrani, *Einrichtung Zur Kleinwinkelstreumessung Zur Analyse Der Nanostruktur an Proben Mittels Röntgenstrahlung*, **2007**, DE102006029449B3.

M. Krumrey, G. Ulm, *Nucl. Instr. Meth. Phys. Res. A* **2001**, *467–468*, 1175–1178.

Primary author(s) : Dr. BRETERNITZ, Joachim (Helmholtz-Zentrum Berlin für Materialien und Energie); Mrs. PALACIOS SAURA, Ana (Helmholtz-Zentrum Berlin; Freie Universität Berlin); Dr. HOELL, Armin (Helmholtz-Zentrum Berlin für Materialien und Energie); Prof. SCHORR, Susan (Helmholtz-Zentrum Berlin; Freie Universität Berlin)

Abstract ID : **98**

OPERANDO CHARACTERIZATION STUDIES OF Ni AND Co BASED AMMONIA DECOMPOSITION CATALYSTS

Tolga Ulucan

The efficient storage of hydrogen in a perspective hydrogen economy is still an unsolved problem. Among others, ammonia (NH3) is regarded as a promising H2 carrier molecule that can be used for the on-site generation of H2 for fuel cells or directly in NH3 solid-oxide-fuel cells. Previous studies on NH3 decomposition catalysts showed high complexity of structure-property relationships. Several factors, e.g., catalyst structure, crystallite size, microstructure, or amorphous phases, can significantly influence the catalytic properties. In this study, Ni and Co catalysts on MgO support were synthesized via the conventional co-precipitation method. 10 and 20 at. % metal loaded catalysts with different pre-conditioning treatments were characterized by several ex-situ methods and tested for their performance in the decomposition of NH3 in a conventional plug-flow reactor.

Operando total scattering experiments during temperature-dependent NH3 decomposition were conducted at P02.1 at DESY. A special gas-flow cell connected to a gas dosing system and a mass spectrometer for product gas analysis has been used.

Ex-situ XAFS experiments were performed at P65 (DESY) to investigate the local structures around Co and Ni atoms. The combination of different characterization data enables structure investigations on different length scales. The structure-performance relations give insights into how different catalysts and processing conditions affect the catalytic activity for NH3 decomposition.

Primary author(s) : ULUCAN, Tolga Han (Max-Planck-Institute für Kohlenforschung); Dr. WEIDENTHALER, Claudia (Max-Planck-Institut für Kohlenforschung); Prof. BEHRENS, Malte (Christian-Albrechts-Universität zu Kiel); Mr. WANG, Jihao (Christian-Albrechts-Universität zu Kiel); Dr. SAHIN, Ezgi (Max-Planck-Institute für Kohlenforschung)

Abstract ID : **99**

Local (de)polarization in Ba(Zr,Ti)O3

Marek Paściak

Inhomogeneous local polarization in ferroelectric materials has become a desired quality leading to enhanced property characteristics, e.g. piezoelectricity, energy storage capacity etc. To characterize nanoscale polarization patterns and to get insight into their dynamics, diffuse scattering (including inelastic neutron scattering) has been extensively used. To facilitate better understanding of diffraction results, we turn to atomistic simulations in which interaction between atoms are represented by classical formulas parametrized on the basis of density functional theory calculations. Here we will present results of such simulations for the classical ferroelectric material $BaTiO_3$ with the titanium atom partially substituted by larger and non-ferroactive zirconium. We will show how Zr brings disruption to the polarization leading to relaxor behaviour, characterized by a nanoscale polarization ordering [1,2]. Long time-period simulations are used to study dynamics of the system on a wide frequency range including both terahertz phonons and sub-terahertz fluctuations of polar clusters. The dynamical structure factor analysis has been performed using the newly developed MP_tools software [3], designed for highly efficient treatment of large-scale molecular dynamics trajectories.

We acknowledge the support of the Czech Science Foundation (CSF project no. 20-20326L)

V. Veerapandiyan et al., Advanced Electronic Materials 8, 2100812 (2022)

J Petzelt et al., physica status solidi (b) 258, 2100259 (2022)

J. Kulda, Acta Cryst. A (2022) in preparation, https://github.com/jkulda/MP_tools.

Primary author(s) : PAŚCIAK, Marek (Institute of Physics of the Czech Academy of Sciences); KULDA, Jiri (Institut Laue Langevin); GONÇALVES, Mauro A. P. (Institute of Physics of the Czech Academy of Sciences); ONDREJKOVIC, Petr (Institute of Physics of the Czech Academy of Sciences); HLINKA, Jiri (Institute of Physics of the Czech Academy of Sciences)

Abstract ID : **101**

Effects of measurement parameters on pair distribution function calculation from in-house total scattering data

Conrad Krämer

With the popularity of pair distribution function analysis rising in recent years, the incentive grows to have easier access to total scattering data. Laboratory scale diffractometers, equipped with Mo or Ag X-ray tubes and detectors with high quantum efficiency have been successfully employed to collect data, qualified for PDF calculations. As the flux of small scale laboratory X-ray sources is magnitudes below those of a synchrotron, measurements may last several days. Here, we use the signal to noise ratio (SNR) of a total scattering experiment as a tool to quantify the required duration of in-house measurements for PDF calculation.

Total scattering diffraction data of alumosilicate iodide sodalite ($|Na_8I_2|[AlSiO_4]_6$) was collected using Ge (1 1 1) – monochromatized Mo radiation (Stoe STADI MP, Debye Scherrer geometry). The sample was filled into a borosilicate glass capillary with an outer diameter of 0.5 mm and a wall thickness of 0.1 mm. Data was collected in the range of 3-120° 2θ ($|Q| = 1534\,pm$) in steps of 0.015° on a Dectris Mythen 1 K position sensitive detector. 168 consecutive measurements of 1 h amounted to a total of 22 h and 16 min of data collection at each angle. By consecutive addition of the intensity data of x measurements we obtained the equivalent of one single measurement with a duration of x hours.

pdfgetx3 was used to calculate the pair distribution function for each total scattering dataset from 1 h to 168 h, using $Q_{max} = 1340\,pm^{-1}$. A routine was developed in python to approximate noise contributions from the measurements and employ them as uncertainties for photon counts, which were propagated as estimated standard deviations to the resulting PDF's. The signal to noise ratio was calculated for every value of background corrected intensity I(Q) and underlying, angle dependent noise. With time as a variable, the mean SNR of the diffractograms is described by a root function. The absolute time-dependent changes of G(r) and refined parameters follow hyperbolic trends towards a respective final, most probable value. This was confirmed by PDF refinements in PDFGUI by a decrease of the residual value R_w from 35.81 % (SNR ≈ 10) to 13.41 % (SNR = 100). Improving the signal to noise ratio beyond 100 did not further improve the fit of G(r).

Primary author(s) : KRÄMER, Konrad

Co-author(s) : GESING, Thorsten M.; ROBBEN, Lars (Uni Bremen)

NEUTRONS FOR SOCIETY
ESRF
ADD2022
ANALYSIS OF DIFFRACTION DATA IN REAL SPACE
16-21 OCT 2022
GRENOBLE, FRANCE

Abstract ID : **103**

D3 at ILL : using polarised neutron to separate coherent, incoherent, and multiple scattering

Anne Stunault

The D3 polarised hot neutron diffractometer at ILL, formerly devoted to magnetism in single crystals, has been upgraded and is now also optimized for studies of liquids over a wide Q-range using polarised neutrons [1]. Within the ILL Endurance program, the instrument has been recently upgraded, with the implementation of a new multi-detector, allowing to measure an average of 3 samples/day.
The method has already been shown to be very powerful in structural studies of molecular liquids or amorphous systems of industrial interest. Here however, after showing the capabilities of the upgraded instrument, we concentrate on some essential "by-products" provided by the incoherent intensities.
Indeed, the spin-incoherent scattering is exactly 3/2 of the measured spin-flip intensity and is here accurately measured. Qualitative analysis shows a gaussian Q-dependence, with a width depending solely on the experimental setup (wavelength, as shown in [2], and detector) rather than the system being investigated. Furthermore, a quantitative analysis allows to devise an empirical model for multiple-scattering, which is always an issue in such strong scatterers as 1H containing systems.

Primary author(s) : STUNAULT, Anne (ILL)

Abstract ID : **105**

Understanding the impact of the gas atmosphere on the thermal deactivation of Pd based three-way catalysts

Sarina-Lena Heck

Introduction

One of the major challenges in today's research on automotive pollution control is thermal deactivation of the catalysts during long term application. Effects such as support segregation, support and noble metal sintering, solid-state reactions and encapsulation are occurring, leading to a decrease of the active surface area and impairing the characteristics of support material [1,2,3,4]. For the three-way catalyst, oxides like γ-Al_2O_3 or CeO_2-ZrO_2 (CZ) are most commonly applied for supporting the active components Pt, Pd and/or Rh [5]. CZ mixed oxides exhibit an oxygen storage capacity (OSC), which is beneficial for balancing out fluctuations in the stoichiometric air-to-fuel ratio (λ =1) needed for an optimal performance of the three-way catalyst [3]. Additionally, CZ mixed oxides can stabilize the noble metal dispersion during catalyst exposure to high temperatures, which is crucial as the sintering of the noble metal particles will not only result in a decrease of the active surface but also in a diminishing of the OSC [1,3,4]. It has been reported that thermal deactivation processes are influenced not only by the aging temperature but also the applied gas atmosphere due to the formation of metallic or oxidized species during the sintering [2,3,6,7]. However, a comprehensive understanding of these phenomena is still missing. Our study focuses on understanding the impact of the gas atmosphere on the aging behavior of Pd-based CeO_2-ZrO_2 catalysts. In-depth characterization coupled with systematic catalytic activity test of the fresh and aged catalysts were conducted.

Results

1 wt.% Pd/CeO_2-ZrO_2 catalysts were prepared by impregnating commercial CeO_2-ZrO_2 with $Pd(NH_3)_4(NO_3)_2$ or $Pd(C_5H_7O_2)_2$ as noble metal precursors, followed by calcination in static air. The resulting powders were aged at 1000 ℃ in oxidizing and inert gas atmospheres. The structural properties of the resulting catalysts were revealed by applying a series of complementary ex situ and in situ characterization methods. Several light-off/light-out cycles were performed while monitoring the gas mixture at the outlet of the catalyst bed by FTIR spectroscopy to assess the catalytic activity.

Due to a slightly smaller particle size and a therefore higher number of active sites, the Pd catalyst prepared with the $Pd(NH_3)_4(NO_3)_2$ solution shows a lower light-off temperature during activity light-off/light-out cycles. However, after treating the catalysts at 1000 ℃ the effect is not visible anymore. Especially aging in inert atmosphere seems to impact the conversion of CO, NO_x and C_3H_6, as all three reactions are only occurring at higher temperatures. A narrowing in the X-ray diffraction patterns after pretreating the catalyst reveals a change in crystallites sizes and therefore a sintering of the support material. After inert atmosphere aging the sample exhibit features of a metallic noble metal species illustrating an increasing of particle size as no noble metal patterns could be identified in the fresh catalyst. This could also be clarified with *ex situ* XANES and EXAFS measurements.

Conclusion

Our systematic study on thermal aging behavior of Pd-based CeO_2-ZrO_2 catalysts contributes to the fundamental understanding of the TWC deactivation processes, as direct correlations between the noble metal dispersion, electronic state and catalyst activity could be revealed. Combined with information on the evolution of the support state, this could be utilized to better predict their activity during long term applications under stochiometric conditions and gain more performance capable emission control catalysts.

References

Wang, J., Chen, H., Hu, Z., Yao, M., Li, Y. *Catal. Rev.*, 57 (2015) 79-144.

Forzatti, P., Lietti, L., *Catal. Today*, 52 (1999) 165-181.

Monte, R.D., Kašpar, J., *Top. Catal.*, 28 (2004) 47-57.

Gänzler, A.M., Casapu, M., Maurer, F, Störmer, H., Gerthsen, D., Ferré, G., Vernoux, P., Bornmann, B., Frahm, R., Murzin, V, Nachtegaal, M., Votsmeier, M., Grunwaldt, J.-D., *ACS Catal.*, 8 (2018) 4800-4811.

Heck, R.M., Farrauto, R.J., *Appl. Catal. A*, 221 (2001) 443-457.

Ogel, E., Casapu, M., Doronkin, D., Popescu, R., Stormer, H., Mechler, C., Marzun, G., Barcikowski, S., Turk, M., Grunwaldt, J.-D., *J. Phys. Chem. C*, 123 (2019) 5433-5446.

He, J.-J., Wang, C.-X., Zheng, T.-T., Zhao, Y.-K., *Johns. Matthey Technol. Rev.*, 60 (2016) 196-203.

Primary author(s) : HECK, Sarina-Lena (Karlsruhe Institute of Technology - Institute for Chemical Technology and Polymer Chemistry)

Co-author(s) : Dr. NAILS, Gülperi (Karlsruhe Institute of Technology - Institute for Chemical Technology and Polymer Chemistry); Dr. DOLCET, Paolo (Karlsruhe Institute of Technology - Institute for Chemical Technology and Polymer Chemistry); Dr. CASAPU, Maria (Karlsruhe Institute of Technology - Institute for Chemical Technology and Polymer Chemistry); Prof. GRUNWALDT, Jan-Dierk (Karlsruhe Institute of Technology - Institute for Chemical Technology and Polymer Chemistry, Karlsruhe Institute of Technology - Institute of Catalysis Research and Technology)

Abstract ID : **106**

Solution of the single crystal diffuse scattering problem using 3D-ΔPDF deconvolution

Arkadiy Simonov

Properties of many materials depend crucially on the structure and distribution of defects in their crystal lattice. Defects can be probed by single crystal diffuse scattering of x-rays or neutrons, however the problem of construction of a model disordered solid consistent with the observed diffuse scattering is still unsolved since currently it relies on either trial-and-error or Patterson function-based methods. Ideally one would seek a method which would allow to solve diffuse scattering in the same sense as direct methods provide a solution to the phase problem of the Bragg peaks crystallography.

In this work we show that such a general method indeed exists for the special case of binary disordered solids. Our method relies on the deconvolution of the 3D-ΔPDF function into two parts: one encoding the structure of the defect, and the other encoding the correlation between defects. The structure of the defect can then be solved by using standard algorithms similar to charge flipping, while the interaction between the defects can be found using the method called the density consistency matching. We illustrate the use of the method using the experimental data from tris-tert-butyl-1,3,5-benzene tricarboxamide single crystal.

Primary author(s) : SIMONOV, Arkadiy

NEUTRONS FOR SOCIETY
ESRF
ADD2022
ANALYSIS OF DIFFRACTION DATA IN REAL SPACE
16-21 OCT 2022
GRENOBLE, FRANCE

Abstract ID : **107**

Insights into the microstructural changes at the Pt/ionomer interface in a fuel cell catalytic ink suspension during the drying process

Sabrina Thomä

Recently, many highly active noble metal catalysts for the oxygen reduction reaction in proton-exchange membrane fuel cells have been developed. However, when applied under working conditions in fuel cells they often suffer of performance loss due to degradation and dissolution. Further, resistancy problems occur at the catalyst/ionomer interface of the thin catalytic layer. (1) In order to tackle this problem and gain control of the structure of the catalyst/ionomer interface, it is of outmost importance to understand the physicochemical phenomena during the various processes of the preparation of the catalytic thin layer, like ink preparation and drying. (2)

Here we present a high-energy in-situ X-ray total scattering study in ESRF-EBS light at ID31 at low (close to grazing) incidence angle whilst drying of a fuel cell catalytic ink suspension on a fused silica substrate. The catalytic ink suspension contains self-synthesized 20 wt% Pt/C catalyst in a water-isopropanol mixture including 5 wt% Nafion solution as ionomer. Upon drying changes in the lattice parameter of the Pt catalyst particles can be tracked suggesting adsorption of the ionomer and changes in electrochemical environment.(3) By comparing the drying process of the ink with and without addition of ionomer and of the catalytic particles in water only, effects from adsorption of ionomer and possible surface oxidation or creation of disordered Pt species will be disentangled.(4) To achieve this goal, first the best-fit Pt model is found and subtracted from the overall signal, and finally by a differential-pair distribution function analysis approach similar to (5) the structural changes of the amorphous components will be analyzed.

On the long run, we want to shed some light on the conformational changes of the ionomer at the Pt/ionomer interface induced by the adsorption to the supported catalyst particles.

1. I. E. Stephens, J. Rossmeisl, I. Chorkendorff, Toward sustainable fuel cells. Science 354, 1378-1379 (2016).
2. S. Woo et al., Current understanding of catalyst/ionomer interfacial structure and phenomena affecting the oxygen reduction reaction in cathode catalyst layers of proton exchange membrane fuel cells. Current Opinion in Electrochemistry 21, 289-296 (2020).
3. R. Chattot et al., Electrochemical Strain Dynamics in Noble Metal Nanocatalysts. J Am Chem Soc 143, 17068-17078 (2021).
4. I. Martens et al., Probing the Dynamics of Platinum Surface Oxides in Fuel Cell Catalyst Layers Using in Situ X-ray Diffraction. ACS Applied Energy Materials 2, 7772-7780 (2019).
5. S. L. J. Thomä, S. W. Krauss, M. Eckardt, P. Chater, M. Zobel, Atomic insight into hydration shells around facetted nanoparticles. Nature Communications 10, 995 (2019).

Primary author(s) : Ms. THOMÄ, Sabrina L. J. (Institute of Crystallography RWTH Aachen University)

Co-author(s) : Dr. DRNEC, Jakub (European Synchrotron Radiation Facility); Prof. ZOBEL, Mirijam (Institute of Crystallography RWTH Aachen)

Abstract ID : **109**

Hydrothermal Injection for Phase-Controlled CaCO3 Synthesis

Adrián Sanz Arjona

Polymorph control has become essential in order to target the desired properties for a given applicability. For instance, calcium carbonate (CaCO3) is well known to be an essential component in nature and can be obtained in three different anhydrous phases: calcite, vaterite and aragonite. Natural biomineralization processes show great polymorph control,1 allowing different CaCO3 phases to serve various purposes in biological organisms.1−3 Increasingly researchers are trying to replicate this same degree of control to develop advanced functional materials by replicating the formation conditions present in nature.

Here we have applied a newly developed hydrothermal injection reactor to the synthesis of CaCO3. This system replicates the hot injection process using only water as a solvent. It allows a similar level of control over nucleation and growth, being considered as analogous to natural mineralisation processes occurring at hydrothermal vents.4 By varying reaction conditions, such as precursor choice, reagent ratios and injection temperature we have shown that this system can achieve a high degree of polymorph selectivity. The phase composition of the samples prepared have been confirmed by Rietveld analysis of the powder X-ray diffraction patterns, and typical morphologies are observed by electron microscopy (SEM). In order to fully represent the relationship of synthetic conditions to the phase of the obtained products we have applied principal component analysis (PCA) to the pair distribution function (PDF) of the powder X-ray diffraction patterns (PXRD). Therefore, a mapping of the optimal conditions needed to obtain each phase and the intrinsic connection of synthesis conditions versus polymorph selection was obtained.

This synthetic approach has been extended to hydroxyapatite [HA, Ca10(PO4)6(OH)2)], considered a bioactive mineral due to its similarity to biological apatite, a constituent of human bones and teeth. Although, HA is not a polymorphic material, it has shown a great range of possible shapes (e.g. needle-like and whisker-like). The control of the shape and size is essential for tuning its properties, like the toughness of the material. Those properties will dictate its potential applicability as a biomaterial.5

1 G. Falini, S. Albeck, S. Weiner and L. Addadi, Science (80-.)., 1996, 271, 67–69.

2 E. Beniash, J. Aizenberg, L. Addadi and S. Weiner, Proc. R. Soc. B Biol. Sci., 1997, 264, 461–465.

3 B. Pokroy, A. N. Fitch and E. Zolotoyabko, Cryst. Growth Des., 2007, 7, 1580–1583.

4 K. Byrappa and T. Adschiri, Prog. Cryst. Growth Charact. Mater., 2007, 53, 117–166.

5 J. Chen, J. Liu, H. Deng, S. Yao and Y. Wang, Ceram. Int., 2020, 46, 2185–2193.

Primary author(s) : Dr. SANZ ARJONA, Adrián (Department of Chemistry, University of Copenhagen)

Co-author(s) : Dr. BATHE, Adrew (School of Chemistry, Trinity College Dublin); Prof. RODRÍGUEZ BLANCO, Juan Diego (Associate Professor, Geology, Trinity College Dublin); Prof. DUNNE, Peter W. (School of Chemistry, Trinity College Dublin)

Abstract ID : **111**

Thermodiffractometry study of (NH4)0.5Co1.25(H2O)2[BP2O8].(H2O)0.5 with CZP framework topology

Mashikoane Mogodi

Four CZP (chiral zincophosphate) zeolite topology compounds with the general formula MIMII (H2O)2[BP2O8].yH2O (MI = Na, NH4 and MII = Mn, Co, y = 0.5, 1) have been prepared under mild hydrothermal conditions (at 180 ℃). Such microporous compounds with aesthetically interesting crystal structures [1] can have interests in fields such as catalysis, storage, separation and ion-exchange. One compound of this family, (NH4)0.5Co1.25(H2O)2[BP2O8].(H2O)0.5, has been studied by variable temperature high resolution powder X-ray diffraction experiments carried out from 298 to 1073 K. Complete Rietveld refinements were achieved by combining stereochemical restraints of the powder diffraction data. At room temperature, this compound crystallizes in the P65 (No. 170) space group with Z = 4 belonging to the hexagonal system. The unit cell parameters obtained were: a = 9.4330(2) Å, c = 15.5203(2) Å, V = 1196.01(5) Å3. The crystal structure consists of a helical anionic framework, ∞[BP2O8]3-, composed of corner sharing BO4 and PO4 tetrahedra. Water and ammonia molecules are found within the helical channels running along the [001] direction. This compound undergoes a series of dehydration, de-ammoniation (analysis augmented by thermogravimetric experiments) and finally diminished sharp Bragg peaks indicating loss of long-range order. Total scattering analysis [2] was applied for the first time coupled to the above conventional structural refinement approach to further unravel this gaseous dissociation and temperature induced amorphization of the rigid host structure. Preliminary X-ray PDF analysis indicates that the local coordination environment found in the low temperature crystalline phases also persists in the amorphous phase.

[1] Kniep, R., Will, H.G., Boy, I. and Röhr, C. Angewandte Chemie International Edition, 1997, 36, 1013.

Egami, T. and Billinge, S.J. Elsevier, 2003.

Keywords: borophosphates, high-temperature, in-situ synchrotron XRPD

Primary author(s) : Dr. MOGODI, Mashikoane Wilson (University of Cape Town)

Co-author(s) : Prof. FERNANDES, Manuel (School of Chemistry, University of the Witwatersrand, Johannesburg, South Africa); Prof. FITCH, Andy (European Synchrotron Radiation Facility (ESRF)); Prof. BILLING, David (School of Chemistry, University of the Witwatersrand, Johannesburg, South Africa)

NEUTRONS FOR SOCIETY
ESRF
ADD2022
ANALYSIS OF DIFFRACTION DATA IN REAL SPACE
16-21 OCT 2022
GRENOBLE, FRANCE

Abstract ID : **112**

Insight into crystallization of Mg-substituted malachite - a precursor to Cu/MgO catalyst for methanol synthesis

Fabio Manzoni

Mixed metal hydroxycarbonates are widely used as precursor materials for tailormade catalysts and can easily be prepared by constant-pH co-precipitation.[1] Precipitation and phase evolution during ageing of mixed Cu,Mg hydroxycarbonates, which are candidates for precursors to Cu/MgO catalysts for CO hydrogenation, have been studied in detail by various methods. The synthesis starts with the co-precipitation of mixed metal nitrate solutions and Na2CO3 at basic pH. An amorphous magnesian georgeite precursor is formed and ageing is needed to yield a crystalline magnesian malachite. With powder X-ray diffraction and pair distribution function (PDF) analysis (measured at ESRF ID31) we were able to track the structural changes during the ageing process of a Cu/Mg 90:10 at.% Cu,Mg hydroxycarbonate. In combination with further methods like atomic absorption spectroscopy and infrared spectroscopy we draw a conclusive picture of the ageing process. We identified the initial precipitation product as magnesian georgeite. Minor side phases of Mg(OH)2, chalconatronite and Na2Zn3(CO3)4 • 3H2O isomorph persist during the ageing process and act as a Mg reservoir until fast crystallization to malachite takes place. Mg is successively built into the amorphous structure, as observed by AAS, pH trend, integral intensity of the (001) reflection of a Mg(OH)2 layered structure and Pearson correlation of the PDFs. PDF refinements (Fig. 1) showed a general match to the georgeite phase, while the short-range order resembles malachite with differently distorted MO6 octahedra for different stages of the crystallization process. Difference-PDFs (dPDF) calculated in between different reaction time intervals allowed us to pin down the structural changes, that seem to be necessary for crystallisation. These includes the built-up of medium-range order in the M (M=Cu,Mg) coordination sphere and inter-connection of MO6 octahedra.

We further studied the calcination of the Mg-substituted malachite to Cu/MgO precatalyst.

With laboratory based XRD and PDF, we found out that the degree of Mg-substitution highly influenced the structure of the formed Cu/MgO precatalyst. Mg-rich samples yielded disordered Cu nanoparticles with amorphous Mg-containing phases. With in-situ synchrotron PDF we now aim to get more insight into the pre-catalyst formation and the underlying mechanisms.

References:

G. Behrendt, B. Mockenhaupt, N. Prinz, M. Zobel, E.J. Ras, M. Behrens, ChemCatChem. 2022, 14, e202200299.

Primary author(s) : MANZONI, Fabio (Institute of Crystallography, RWTH Aachen University)

Co-author(s) : PRINZ, Nils (Institute of Crystallography, RWTH Aachen University); BEHRENDT, Gereon (Institute of Inorganic Chemistry, University of Duisburg-Essen); Prof. BEHRENS, Malte (Institute of Inorganic Chemistry, Christian-Albrecht University of Kiel); Prof. ZOBEL, Mirijam (Institute of Crystallography, RWTH Aachen University)

Abstract ID : **113**

Comprehensive characterization of ternary quantum dots by reciprocal-space X-ray total scattering methods

Mara Colombo

Amidst the plethora of potential applications of semiconducting nanomaterials, the use of heavy metal ions and corresponding toxicity is under scrutiny in the case of designing daily-life commodities. In the quest for quantum dots with greener formulation, Cu-based materials turn out to be potential candidates and, in this regard, ternary chalcogenide quantum dots (QDs) remain in the limelight for the last few years.1-2 The main advantage beyond the development of nanostructured semiconductors is the opportunity to finely tune their optical and electronic properties by modifying their structural and microstructural features. This sparked the development of colloidal synthesis approaches that enable ultra-precise control of the size and morphology of particles to the nanoscale.
Nonetheless, the investigation of surface structure and defects remains highly challenging due to the lack of established analytical approaches. This is a concerning limiting factor that likely hinders further developments in the field for the lack of a complete and reliable description of the target systems on a length scale that spans from the atomic to the nano-range.
Our group has already tackled this problem by successfully combining reciprocal space X-ray total scattering techniques in the wide- (WAXS) and small-angle regions (SAXS) to achieve a detailed characterization of size, morphology, and defects in PbS, and zinc blende CdSe QDs.3
We are now focusing our attention on CuInS2 as a promising alternative to more well-known QDs, that possess favorable photophysical properties combined with low toxicity.

Starting from previously established synthesis routes, we have refined a colloidal synthesis approach to obtain QDs with tightly selected size and morphology. This can be conveniently achieved by tuning the reaction conditions, such as – reaction time, concentration ratio of capping agent, source of chalcogens, ratio of precursor's concentration.4 As for example, CuInS2 can be synthesized following high-temperature colloidal pathways using octadecene as solvent, oleic acid (OA) as capping agent, and dodecane thiol (DDT) as sulfur source. The morphology of the quantum dots can be tuned by changing the ratio of OA and DDT. Additionally, by changing the ratio of two precursors, i.e., copper acetate and indium acetate, we can tune the optical properties of the products.
The purification protocol was specially designed to enable the size selection of the QDs. The process was closely monitored by a combination of laboratory X-ray diffraction and absorption/emission spectroscopies.
Finally, a thorough structural and microstructural characterization of the QDs was carried out by SAXS/WAXS reciprocal space total scattering methods, based on the Debye Scattering Equation (DSE).5
The results of this study may serve as an important reference point to further the understanding of the connection between the structural and functional properties of this important class of materials.

Acknowledgements
We thank the Fondazione Cariplo, CubaGREEN Project 2020-4382 for financial support.

References

1. W. v. d. Stam, A. C. Berends and C. d. M. Donega, Chem Phys Chem., 2016, 17, 559–581.
2. D. Aldakov, A. Lefrançoisa and P. Reiss, J. Mater. Chem. C, 2013,1, 3756–3776.
3. F. Bertolotti et al, Nature Mater. 2016, 15, 987-994; D. Moscheni et al, ACS Nano., 2018, 12, 12558–12570.
4. J. Kolny-Olesiak and H. Weller, ACS Appl. Mater. Interfaces., 2013, 5, 23, 12221–12237; C. Coughlan et al., Chem. Rev. 2017, 117, 5865–6109.
5. Cervellino et al. J. Appl. Cryst. 2015. 48, 2026–2032; F. Bertolotti et al, Eur. J. Inorg. Chem. 2018, 3789–3803.

Primary author(s) : DENGO, Nicola (University of Insubria and To.Sca.Lab); Dr. COLOMBO, Mara (Univer- sity of Insubria and To.Sca.Lab); ROY, Shilaj (University of Insubria and To.Sca.Lab); ANZINI, Pietro (University of Insubria and To.Sca.Lab); FERRI, Fabio (University of Insubria and To.Sca.Lab); MASCIOCCHI, Norberto (Univer- sity of Insubria and To.Sca.Lab); GUAGLIARDI , Antonietta (University of Insubria and To.Sca.Lab); BERTOLOTTI, Federica (University of Insubria and To.Sca.Lab)

Abstract ID : **122**

Nanobeam X-ray PDF analysis of the amorphous calcium carbonate phases in Pinctada Margaritifera shells

Stefano Checchia

The development of bio-inspired mineralization strategies to obtain tough and gossamer materials relies on the quantitative description of biomineralization mechanisms. For most crystalline biominerals a granular organization involving different polymorphs suggests a different mechanism than classical crystallization theory and recent research pointed to the important role of the amorphous calcium carbonate (ACC) precursors in the formation of calcareous biominerals. Crucially, biogenic ACC is often found in the final mineralized state, which enables the study of the transient states of biomineralization. The multiple crystalline and amorphous compounds present in many biominerals, however, represent a problem for the selective experimental characterization of the amorphous fraction. As a result, analysis has mostly centered on spectroscopic techniques that, while adding key insights into local bond structures, cannot spatially resolve the species at play.
In this work we used nanobeam X-ray total scattering, together with a novel approach to separate crystalline and amorphous scattering contributions [1], to obtain a spatially-resolved atomic pair distribution function (PDF) from the shell of the oyster *Pinctada margaritifera*. Through multivariate analysis and Reverse Monte Carlo modelling, we resolve three distinct ACC compounds and show that these differ mostly in their spatial distribution and Ca-O nearest-neighbor distance. Further characterization by Stimulated Raman spectroscopy and micro-Raman [2] evidenced the role of Mg in the structural fluctuations and ultimately suggested a Mg-mediated crystallization pathway.

1. T.A. Grünewald, S. Checchia, V. Chamard, et al., PNAS, under review
2. J. Duboisset, et al., Acta Biomaterialia 142 (2022)

Primary author(s) : CHECCHIA, Stefano (ESRF)

Co-author(s) : GRÜNEWALD, Tilman (Aix-Marseille Univ, CNRS, Centrale Marseille, Institut Fresnel); CHAMARD, Virginie (Aix-Marseille Univ, CNRS, Centrale Marseille, Institut Fresnel); DI MICHIEL, Marco (ESRF)

Abstract ID : **124**

Machine learning based approach for solving atomic structures of nanomaterials combining pair distribution functions with density functional theory

Magnus Kløve

Structural characterization of function materials are crucial, as materials' properties are intimately linked to their atomic structures. Since X-ray and neutron scattering techniques are direct probes for the atomic arrangements of solids, the crystal structures of unknown compounds can easily be determined from single crystal diffraction data – and with care from high-quality powder diffraction data on well-crystalline powder samples as well. Real functional materials, however, are not necessarily well crystalline, but are likely to be nanostructured and so the traditional crystallographic structure solution approaches fail.

The pair distribution function (PDF) analysis of X-ray and neutron total scattering data is a valuable tool for studying nanomaterials, but PDF analyses are often carried out as real-space counterparts to Rietveld refinements, i.e. where a priori structural information is a necessity. However, there is a need for solving the atomic structure of truly unknown nanocrystalline phases in the absence of any efficient and versatile procedures.

Here, we present an efficient machine-learning enhanced global optimization algorithm capable of solving the atomic structures of functional materials from their experimental PDFs. By combining DFT energy evaluations of candidate structures with their agreement factor (Rw) from PDF modelling, the algorithm efficiently performs a global optimization in an on-the-fly, machine-learning trained DFT+PDF surrogate landscape, thus solving the atomic structure from the PDF.

Primary author(s) : KLØVE, Magnus (Aarhus University)

Co-author(s) : DONONELLI, Wilke (University Bremen); Prof. IVERSEN, Bo Brummersted (Aarhus University)

NEUTRONS FOR SOCIETY
ESRF
ADD2022
Analysis of Diffraction Data in Real Space
16-21 Oct 2022
Grenoble, France

Abstract ID : **125**

Total scattering and pair distribution function studies of TiO2-bronze nanocrystals as electrodes in Li-ion batteries

Martin Karlsen

The polymorphs of TiO2 constitute a large and diverse family of material structures. For application as negative electrodes in Li-ion batteries, especially the bronze polymorph of TiO2 has received significant attention due to attractive features including low intercalation potential, high reversibility, and high current performance [1]. However, the attention has been given to crystalline states of TiO2-bronze, where conventional powder diffraction techniques combined with Rietveld refinement provide information on the long-range ordered, crystalline structure of the material. Instead, the focus here is on TiO2-bronze nanocrystals that are approximately 3, 5, and 7 nm in size, which limits the information extractable using more conventional powder diffraction methods. Total scattering and pair distribution function (PDF) analysis offer unique insights into the atomic and nano scale structures of these nanosized materials that are characterized ex-situ as well as operando. Elucidating the structural evolution from the PDF data during charge and discharge is aided by the recently offered tools of 'PDF in the cloud' at pdfitc.org[2], which are used for phase identification via structureMining[3], for examination of reversibility using similarityMapping, and for exploration of the phase behavior during charge and discharge through nmfMapping[4,5]. This poster will illustrate how these various analysis approaches can be used as the basis of the modelling of the PDF data using DiffPy-CMI[6] to describe the novel insight gained about the TiO2-bronze nanocrystals as electrode in Li-ion batteries.

Aravindan et al., Materials Today (2015), 18, 345-351.

Yang et al., Acta Cryst. (2021). A77, 2-6.

Yang et al., Acta Cryst. (2020). A76, 395-409.

Liu et al., J. Appl. Cryst. (2021). 54, 768-775.

Thatcher et al., Acta Cryst. (2022) A78, 242-248.

Juhás et al., Acta Cryst. (2015). A71, 562-568.

Primary author(s) : KARLSEN, Martin (University of Southern Denmark); Prof. DE ROO, Jonathan (University of Basel); Prof. BILLINGE, Simon (Columbia University + Brookhaven National Laboratory); Prof. RAVNSBÆK, Dorthe Bomholdt

Abstract ID : **126**

Studying the spin-liquid behavior in Mg2Ho3Sb3O14 and derivatives

Pragati Pherwani

Kagome structures are triangular lattice structures exhibiting frustrated magnetism due to geometry. A three-dimensional analogue of the Kagome lattice is the pyrochlore lattice (represented as A2B2O7) which is constructed from corner sharing tetrahedra. Zhao-Feng Ding, et. al, have studied, Pyrochlore lattices (space group Fd-3m) containing A and B type of cations (magnetic, non-magnetic ions) that are stacked alternatively as A3B and B3A layers. By selective doping of nonmagnetic ions (e.g., Zn2+), two-dimensional Kagome lattice can be isolated from the pyrochlore lattice. Z. L. Dun, et. al also studied , in the Tripod Kagome Lattice (TKL) compound, spins remain entangled and do not order in the zero-temperature limit. Therefore, the kagome compounds are potential candidates for quantum spin liquid.

We aim to scrutinize the structural and physical properties of A2R3Sb3O14 (A = Mg,Zn,Co,Ca ; R = Ho,Pr,Y). The scope of the study includes magnetic and transport properties along with crystal structure and magnetic structure of these compounds. We have prepared Mg2Ho3Sb3O14, Zn2Ho3Sb3O14, Co2Ho3Sb3O14, Ca2Pr3Sb3O14 compounds by solid-state reaction method and the XRD study shows that the majority phase is Mg2Ho3Sb3O14,(Mg-Ho) with some impurity phase, Zn-Ho in single phase whereas Co-Ho and Ca-Pr are still under study. Magnetization study for Zn-Ho has been carried out by employing Physical Properties Measuring Systems (PPMS) with a magnetic field of 1000 Oe in the temperature range of 3K to 300K. No magnetic ordering was observed down to 3K The temperature-dependent neutron diffraction by employing a powder neutron diffractometer (PD-3) is underway. Analysis of temperature-dependent neutron diffraction will lead us to understanding of magnetism involved. Through this systematic study, we also intend to explore the quantum spin liquid state in these compounds.

Primary author(s) : Ms. PHERWANI, PRAGATI; Dr. KAUSHIK, S. D

NEUTRONS FOR SOCIETY
ESRF
ADD2022
ANALYSIS OF DIFFRACTION DATA IN REAL SPACE
16-21 OCT 2022
GRENOBLE, FRANCE

Abstract ID : **127**

Correlation between composition of the Cd0.80-yMn0.20ZnyTe (y=0.05-0.15) crystals and their structure

Vasylyna Kopach

Diluted magnetic semiconductors Cd0.80-yMn0.20ZnyTe (y=0.05-0.15) have been grown in the zinc-blende structure using a vertical Bridgman method. With the help of XRD analysis by the Rietveld method, the value of the lattice constant of Cd0.80-yMn0.20ZnyTe (y=0.05-0.15) ingots (y = 0.05–0.15) was calculated. It was determined that the value of the lattice constant linearly decreases from 6.41(6) to 6.37(5) Å with increasing of ZnTe concentration. The powder diffractograms of the studied samples agree well with the patterns of Cd0,45Mn0,35Zn0,20Te and Cd0,60Mn0,35Zn0,05Te [1]. This indicates the same crystal structure of the compared samples. Using the SEM-EDX and XRF analyses, the molar ratio of the amounts of elements was obtained. The typical IR microscope images of all as-grown crystals show that the size of Te inclusions was about 5-20 ▯m. By measuring the transmission spectra, it was established that the width of the band gap of the grown semiconductor crystals increases linearly with an increase in the amount of ZnTe.

[1] Y. Hwang, S. Chung, and Y. Um, Phys. Stat. Solid. Vol. 4, №12 (2007), p.4457–4460.

Primary author(s) : Mrs. KOPACH, Vasylyna (Yuriy Fedkovych Chernivtsi National University); Dr. KOPACH, Oleh (Yuriy Fedkovych Chernivtsi National University); Prof. FOCHUK, Petro (Yuriy Fedkovych Chernivtsi National University)

Abstract ID : **128**

An approach towards co-production of hydrogen and carbonaceous material as valuable products via thermo-catalytic conversion of plastic waste using Ce doped SnO2 nanoparticles.

Bhawna Bhawna

Pyrolysis of polypropylene (PP) plastic has been performed with Ce doped SnO2 (Ce:SnO2) nanoparticles (NPs) with a remarkable production of hydrogen gas. To achieve the maximum production of gas, SnO2 was doped with different concentrations of Ce i.e., 2%, 4%, 6% and 8%. In spite of that, to understand the effect of Ce doping in SnO2, the results were compared with pure SnO2. Significant hydrogen gas was produced on performing the pyrolytic reaction with 6% Ce:SnO2. Reaction conditions were altered in terms of heating rate and temperature to investigate the effect on CNT production. A maximum carbonaceous CNT production was obtained when the heating rate was kept to 30°/min. Temperature profile indicated that the effective hydrogen gas and CNT were collected at a lower temperature of 350°C which are generally the products of reactions at higher temperature. The synthesized catalyst and the carbonaceous CNT were characterized through different techniques such as- XRD, SEM, TEM, TGA. The research enlightens the beauty of facile synthesized doped metal oxides to sustain the pyrolytic conversion of plastic waste at lower temperature into value added products.**

Primary author(s) : Ms. BHAWNA, Bhawna (M.Sc.); Dr. KUMAR, VINOD (Ph.D.); Prof. SINGH, PRASHANT (Ph.D.)

NEUTRONS FOR SOCIETY
ESRF
ADD2022
ANALYSIS OF DIFFRACTION DATA IN REAL SPACE
16-21 OCT 2022
GRENOBLE, FRANCE

Abstract ID : **129**

Orientation mapping of cholesterol monohydrate in gallstones utilizing X-ray diffraction tensor tomography

Ingvild Hageberg

Gallstones are pathological formations affecting people across the world and so they are an interest of research. Despite the relatively high prevalence of gallstones, the formation of gallstones, in particular the microstructural nucleation events, remains less understood. As the delicate balance in the gallbladder becomes unstable either from environmental or genetic factors, nucleation events occur that can produce crystals. There are two types of gallstones: cholesterol and pigment stones. Pigment stones are made of different mixtures of calcium bilirubinate, calcium, copper, and mucin glycoproteins, while cholesterol stones are mostly made of pure cholesterol crystals.

X-ray diffraction tensor tomography (XRD-TT) is a newly developed imaging methodology that facilitates 3-dimensional imaging with chemical as well as orientational contrast. This methodology has been used to study the orientational information of cholesterol monohydrate crystallites present within human gallstones and to visualize their preferred orientation. The diffraction pattern indicates the presence of oriented cholesterol monohydrate within the gallstones, without the presence of any other mineral. The 001 and 002 diffraction peaks were utilized for the XRDTT analyses. Complementary, attenuation-based µCT experiments have been performed to understand the internal structures of the studied gallstones i.e., morphology, porosity, and density variations. The study demonstrates the unique capability of XRD-TT in studying 3D orientational information which is expected to provide new insights into the process of pathological mineralization.

Primary author(s) : Ms. HAGEBERG, Ingvild Uri (Norwegian University of Science and Technology)

Co-author(s) : Dr. MÜRER, Fredrik K. (SINTEF Helgeland); Mr. YOUNAS, Daniyal (Norwegian University of Science and Technology); Dr. SHEIDL, Katharina (Norwegian University of Science and Technology); Dr. DI MICHIEL, Marco (ESRF); Dr. CHUSHKIN, Yuriy (ESRF); Dr. CHATTOPADHYAY, Basab (Norwegian University of Science and Technology); Prof. BREIBY, Dag Werner (Norwegian University of Science and Technology)

Abstract ID : **130**

New Insight into Formation of Copper Oxide Based Nanocomposite to Boost Photocatalytic Water Splitting for Generation of Dihydrogen

Sanjev Kumar

Solar energy and light have been the source of sustenance of life on earth. Photocatalytic processes such as photosynthesis are cornerstones of our energy sources whether in terms of food or fuel. However, as human population multiplies exponentially, the anthropogenic stress on our natural resources is manifesting in alarming forms [1, 2]. Conventional fossil fuels such as coal and petroleum have been the primary source of energy for millennia but their dwindling availability and generation of by-products such as greenhouse gases including carbon dioxide, not only leave us with the challenge of finding alternative energy sources but also to explore avenues to remedy the harm already caused in our ecosystems due to pollution and global warming [3]. To overcome these circumstances, "Alternative Energy Resources" is the necessity of the hour. Dihydrogen is a non-polluting alternative fuel because it contains more energy as compared to petroleum and has the highest calorific value of any other fuels [4].

The synthesis of copper oxide-based nanocomposite was done via wet chemical method. The nanocomposite performs as a photocatalyst for generation of H2 gas through water splitting technique with NiO as co-catalyst and MeOH as sacrificial agent. Various characterization techniques such as X-ray diffraction (XRD), Scanning electron microscopy (SEM), Fourier-transform infrared spectroscopy (FTIR), and X-ray photoelectron spectroscopy were used for the detailed study of nanocomposite.

Keywords: Nanocomposite, Photocatalyst, Water Splitting, Sacrificial Agent.

References

1. Creutzig, F., et al., The underestimated potential of solar energy to mitigate climate change. Nature Energy, 2017. 2(9): p. 1-9.
2. van Ruijven, B.J., E. De Cian, and I.S. Wing, Amplification of future energy demand growth due to climate change. Nature communications, 2019. 10(1): p. 1-12.
3. Shehzad, N., et al., A critical review on TiO2 based photocatalytic CO2 reduction system: Strategies to improve efficiency. 2018. 26: p. 98-122.
4. Yamada, Y., et al., Cu/Co3O4 nanoparticles as catalysts for hydrogen evolution from ammonia borane by hydrolysis. The Journal of Physical Chemistry C, 2010. 114(39): p. 16456-16462.

Primary author(s) : Mr. KUMAR, SANJEEV (DEPARTMENT OF CHEMISTRY, UNIVERSITY OF DELHI)

Co-author(s) : Dr. BHARTI, AKHILESH (DEPARTMENT OF CHEMISTRY, KIRORI MAL COLLEGE); Dr. KUMAR, VINOD (SPECIAL CENTRE FOR NANOSCIENCE)

Abstract ID : **131**

How reliable is the pair distribution function for in situ studies of hydrothermal reactions?

Rasmus Christensen

In recent years, *in situ* X-ray total scattering experiments has become a widespread technique for studying particle formation from solution, as it uniquely probes the changes to the local structure, independent on crystallinity. Pair distribution analysis allows for the extraction of the structural motifs formed during a hydrothermal reaction which then provide information regarding the reaction mechanism.
The extracted modelling parameters from an *in situ* total scattering experiment (*e.g.*, Particle size) is usually evaluated using the standard deviation. However, the standard deviation is the uncertainty of the model, and the true experimental uncertainty is unknown.
In this study, the hydrothermal reaction of $ZrCl_4$ in H_2O was studied using *in situ* X-ray total scattering. A total of 10 repetitions of the experiment were performed to study the reliability of the experimental technique as well as elucidating pitfalls related to the data processing of an *in situ* total scattering experiment.

Primary author(s) : Mrs. CHRISTENSEN, Rasmus (Aarhus University)

Co-author(s) : Prof. IVERSEN, Bo Brummersted (Aarhus University); Mr. KJÆR, Magnus Kløve (Aarhus University)

NEUTRONS FOR SOCIETY
ESRF
ADD2022
ANALYSIS OF DIFFRACTION DATA IN REAL SPACE
16-21 OCT 2022
GRENOBLE, FRANCE

Abstract ID : **132**

X-ray investigation of MnS nanocrystals

Viktoriia Pylypko

Manganese sulfide (MnS) is an important semiconductor material due to its optical, electric, and magnetic properties combination and potential applications in solar cells as a window/buffer material, optoelectronic devices, and electrode material. It is well known that bulk MnS has three different crystal structures: stable α-MnS, metastable β-MnS, and γ-MnS structures. Nanosized MnS had attracted growing interest for this material in last time also. Depending on the nanocrystals (NCs) preparation thermodynamic conditions it is possible to obtaine NCs with different morphologies and crystal structures.
However, there are few studies to investigate the influence of the solvent type on the morphology and phase structure of MnS NCs. Using a wet chemical pattern we investigated the influence of solvents nature (aqua and polar organic substances) on the crystal structure of the MnS NCs in our work. Manganese acetate (Mn(CH3COO)2), and Sodium sulfide (Na2S*9H2O) with different solvents such as acetone, ethanol, and ethylene glycol (EG) were used for the synthesis.
The phase structures of the as-prepared product were investigated using the powder X-ray diffraction (XRD), energy-dispersive spectrometer (EDS), and atomic force microscopy (AFM). Optical properties were investigated by photoluminescence spectra (PL).
The conducted studies confirmed the significant influence of the solvent nature on the crystalline structure of the obtained nanoparticles, and confirmed the formation of γ-MnS or β-MnS or a mixture of two modifications with different parameters of the crystal lattice [1].

[1] Zhang J. et al.: Solvothermal synthesis of manganese sulfides and control of their phase and morphology. J. Mater. Res. Vol.33, Issue 24 (2018). P.4224-4232.

Primary author(s) : Mrs. PYLYPKO, Viktoriia (author); Prof. FOCHUK, Petro (co-author)

Abstract ID : **134**

Self-assembly long-acting injectable peptide hydrogels for HIV/AIDS treatment and prevention

Yuming An

Introduction: Eradicating HIV/AIDS by 2030 is a central goal of the World Health Organisation. However, patient compliance with most approved HIV/AIDS treatments is low due to the complexity of drug dosing. The development of a simple, long-term formulation can be an effective way to overcome this challenge. Our team is working on a long-acting peptide-based drug delivery platform, which is injected into the skin or muscle. We aimed to prepare an in situ hydrogel which capable of self-assembly in response to phosphatases present in the subcutaneous or intramuscular. Zidovudine is a model drug covalently bound to our peptide by an ester-drug bond.

Methods: Solid-phase synthesis technology is used to prepare D, L-α peptide, NapffkY(p)G-OH. Zidovudine is modified with N-hydroxysuccinimide to form an ester bond to conjugate with peptide. The mechanical properties of the gel were studied using oscillatory rheology (time, frequency, strain sweeps). The underlying structure of hydrogel fibre networks were studied using circular dichroism and small angle neutron scattering (SANS) at ILL, Grenoble. *In vivo* zidovudine drug plasma concentrations was obtained across 35 days in Sprague Dawley rats after subcutaneous administration of Napffk(AZT)Y(p)G-OH.

Results: Rheology studies showed that peptides conjugated with zidovudine rapidly formed hydrogels after activated by 2U phosphatase SANS demonstrated peptide gels closely fit model data for the flexible cylinder elliptical model. The presence of entangled gel fibres also suggests a large component of gel stiffness/strength that can be controlled by external conditions e.g. the gelation/formulation process. *In vivo* studies showed that plasma concentrations of zidovudine were maintained at 35 days post-dose (IC 5030-130 ng/ml).

Conclusion: This study is to develop a novel peptide hydrogel with a long-acting, peptide-based, injectable drug delivery platform which can be used in HIV/AIDS treatment and prevention. In future work, we will introduce contraceptive drugs to combine in the product to enrich the scope of application.

Primary author(s) : AN, Yuming

Co-author(s) : Dr. PENTLAVALLI, Sreekanth (Queen's Universtiy Belfast); Dr. COULTER, Sophie (Queen's University Belfast); Dr. CROSS, Emily (Queen's University Belfast); Dr. VORA, Lalitkumar (Queen's University Belfast); SCHWEINS, Ralf; Dr. LAVERTY, Garry (Queen's University Belfast)

NEUTRONS FOR SOCIETY
ESRF
ADD2022
ANALYSIS OF DIFFRACTION DATA IN REAL SPACE
16-21 OCT 2022
GRENOBLE, FRANCE

Abstract ID : **135**

Formation mechanisms for multi-metallic and high entropy alloy nanoparticles: When do metals mix?

Tobias Mølgaard Nielsen

High Entropy Alloys (HEAs) have become an increasingly interesting subject of research for their use as catalysts. One of the advantages of HEAs compared to their bi- and trimetallic counterparts stem from the increased configurational entropy, resulting in excellent stability. (1, 2) In order to optimize the catalytic properties, it is necessary to be able to control the composition of the HEAs and to understand how different synthesis parameters affect the crystal structure of the HEA nanoparticles (3).

We here present results from a project, whose aim is to investigate how the synthesis strategy and method affects which HEA compositions can be obtained, and how the number of metals in the compound affect the mixing or metal segregation. By comparing theoretical calculations to results from colloidal syntheses (4), we will map which alloys can be formed and investigate how well we can predict the formed phases, depending on the metals included. The particles are characterized using Powder X-Ray Diffraction (PXRD) and X-Ray Fluorescence (XRF). We also dive deeper into the formation mechanism of single-phase fcc multi-metallic and HEA nanoparticles by doing combined in situ XRD and XANES studies utilizing synchrotron radiation. Through these experiments, we hope to gain a better understanding of the limitations of HEA formation, and to investigate how to alter the composition of HEAs by changing synthetic parameters.

1. G. M. Tomboc, T. Kwon, J. Joo and K. Lee, Journal of Materials Chemistry A, 2020, 8, 14844- 14862.
2. D. B. Miracle and O. N. Senkov, Acta Materialia, 2017, 122, 448-511.
3. S. Li, X. Tang, H. Jia, H. Li, G. Xie, X. Liu, X. Lin and H.-J. Qiu, Journal of Catalysis, 2020, 383, 164- 171.
4. M. Ishijima, J. L. Cuya Huaman, H. Wakizaka, K. Suzuki, H. Miyamura and J. Balachandran, Inorganic Chemistry, 2021, 60, 14436-14445.

Primary author(s) : Mr. MØLGAARD NIELSEN, Tobias (University of Copenhagen)

Co-author(s) : Dr. MATHIESEN, Jette Katja (University of Copenhagen); Mr. MØGELBERG CLAUSEN, Christian (University of Copenhagen); Dr. DRATH BØJESEN, Esben (Aarhus University); Prof. ROSSMEISL, Jan (University of Copenhagen); Dr. ØRNSBJERG JENSEN, Kirsten Marie (University of Copenhagen)

NEUTRONS FOR SOCIETY
ESRF
ADD2022
ANALYSIS OF DIFFRACTION DATA IN REAL SPACE
16-21 OCT 2022
GRENOBLE, FRANCE

Abstract ID : **145**

In-operando Pair Distribution Function and Small Angle X-ray Scattering of electrocatalytic processes

Stefanie Punke

To engineer the next generation catalysts, an understanding of the current catalyst's activation and degradation process is essential. This has been proved to be very difficult to achieve so far [1]. This poster will present a way to follow these processes under electrochemical conditions.

The method to achieve this is a setup where combined in-operando Pair Distribution Function (PDF) and Small Angle X-ray scattering (SAXS) is possible. The PDF will give insights on the atomic pair distances and the range of order within the crystalline domains. Modelling of the PDF can be used to determine the chemical composition, the structure, and give an estimate of the crystallites' size. With the help of SAXS, the overall nanoparticles' form and size distribution can be determined. The combination of both allows to follow changes in the morphology and composition of the catalyst directly. Additionally, the measurement of the electrochemical performance allows to directly correlate observed differences in the performance to the structural changes.

With this knowledge of the activation and degradation processes, important insights to the catalysts' behaviour can be gained. Eventually, these insights could help to improve the efficiency of the next generation catalyst and to move away from expensive and rare materials.

[1] I. Martens, R. Chattot, J. Drnec, Decoupling catalyst aggregation, ripening, and coalescence processes inside operating fuel cells, Journal of Power Sources 521 (2022).

Primary author(s) : PUNKE, Stefanie (University of Copenhagen); Dr. PITTKOWSKI, Rebecca K. (University of Copenhagen); JENSEN, Kirsten Marie (University of Copenhagen); Prof. ARENZ, Matthias (University of Bern); KIRKENSGAARD, Jacob J. K. (University of Copenhagen)