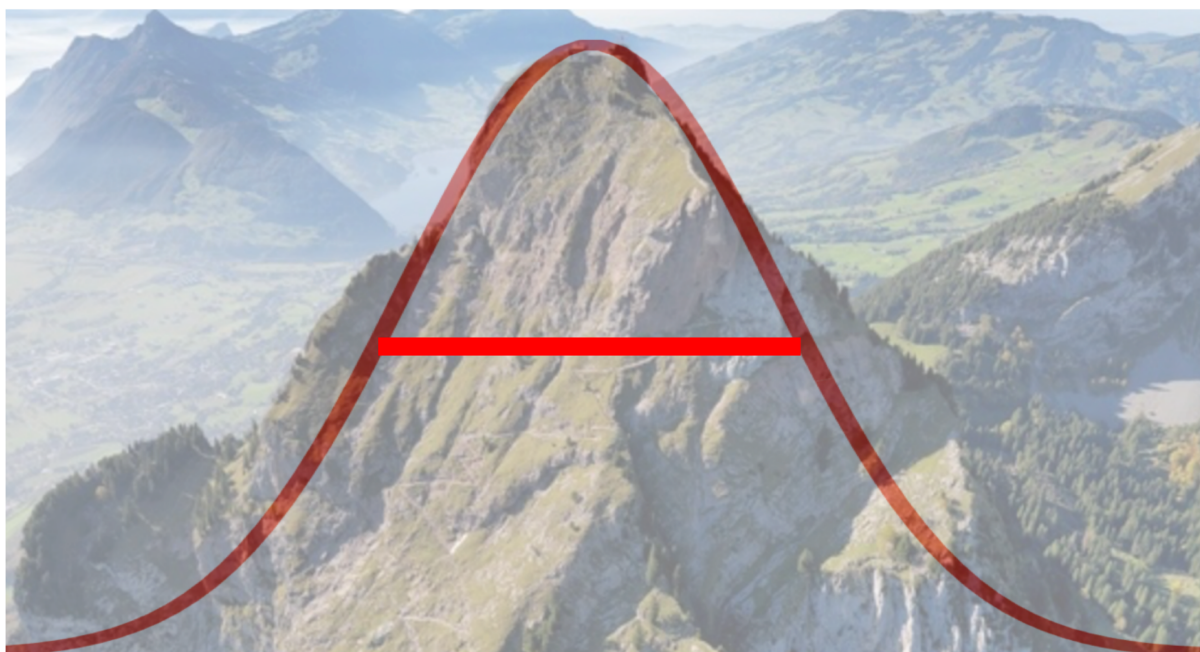


Swiss Crystallographic Society Annual Meeting 2018  
Paul Scherrer Institute, VILLIGEN  
September 11-12, 2018

## *The Breadth of Crystallography*



$$D = k\lambda / \beta \cos \theta$$


# Scientific Program

## SGK-SSCr Annual Meeting - Wednesday 12<sup>th</sup> September 2018

Villigen PSI 5232, Auditorium WHGA/001

<b>09:30 – 09:50</b>		<b>Registration &amp; Welcome Coffee</b>
<b>09:50 – 10:00</b>	<i>P. Macchi (U Bern) A. Cervellino (PSI)</i>	<b>Welcome Address</b>
<b>10:00 – 11:50</b>	<b>Session 1</b>	<b>Chair: A. Cervellino</b>
10:00 – 11:00	<i>Dr. Ing. Hans Scheel, (General Protection Engineering GmbH)</i>	Invited Lecture #1 "Crystal Growth and Crystal Technology"
11:00 – 11:25	<i>Prof. Hans Grimmer (PSI)</i>	Oral contribution #1 "DFT Calculations of Twin Boundaries in KLiSO <sub>4</sub> "
<b>11:25 – 12:15</b>		<b>Lunch – Poster Session</b>
<b>12:15 – 14:00</b>		<b>General Assembly of the SGK-SSCr</b>
<b>14:00 – 15:50</b>	<b>Session 2</b>	<b>Chair: N. Casati</b>
14:00 – 15:00	<i>Prof. Wendy Lee Queen (EPFL Valais)</i>	Invited Lecture #2 TBA
15:00 – 15:25	<i>Prof. Radovan Cerny (U Geneva)</i>	Oral contribution #3 "Metal Hydro-Borates for Li- and Na-ion Batteries"
15:25 – 15:50	<i>Dr. Amin Sadeghpour (EMPA)</i>	Oral contribution #4 "The Semi-crystalline Structural Features Revealed by Diffractions at Small Angle Regime"
<b>15:50 – 16:10</b>		<b>Coffee Break – Poster Session</b>
<b>16:10 – 18:15</b>	<b>Session 3</b>	<b>Chair: R. Sibille</b>
16:10 – 17:10	<i>Prof. Johan Chang (U Zurich)</i>	Invited Lecture #3 "Energetics of Lattice and Electronic Degrees of Freedom"
17:10 – 17:35	<i>Dr. Sumit Maity (PSI)</i>	Oral contribution #4 "Neutron diffraction studies of oxygen disorder in Nd <sub>2</sub> NiO <sub>4</sub> +d"
17:35 – 18:00	<i>Dr. Zoltan Balogh-Michels (EMPA)</i>	Oral contribution #5 "Crystallinity and crystallite size determination of recrystallized nanocellulose"
18:00 – 18:15		Poster prize ceremony & Farewell

# ***Abstracts***

## ***1. Plenary lectures***

## Crystal Growth and Crystal Technology

Hans J. Scheel

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The invention of the germanium transistor in 1947 and subsequently the silicon transistor in 1954 initiated the solid-state electronics revolution based synthetic crystal and epitaxial layer (epilayer) production including crystal machining (sawing, polishing etc.). This crystal technology allowed the development of all aspects of modern communication, global commerce, medical technology and energy production.

In connection with the discovery of new materials, for instance ferroelectric materials at ETH Zurich with Paul Scherrer and Georg Busch who, in 1935, discovered ferroelectric KDP, crystals of high quality were required for research. Also, ferromagnetic, laser, superconducting materials and compound semiconductors were of interest, and phase transitions in general developed as a topical research field with the need for crystals. Not only universities, but also industrial research laboratories and national and military research laboratories established crystal growth facilities in the 1960s.

Initial crystal growers often kept their process secret. A problem with many crystal growers was, and still is, that often they apply a crystal growth method which is not optimum leading to unsatisfactory results with respect to size and quality of crystals. Only with high-quality crystals and their sufficient characterization can reproducible physical properties be achieved.

The science of crystal growth developed slowly and was assisted by the Journal of Crystal Growth and by national and international conferences. The first ICCG met in Boston in 1966 and the second in Birmingham, UK in 1968. National and international crystal growth societies were formed, in Switzerland as a joint Society of Crystallography and Crystal Growth 1969 with initiators Nowacki in Berne, Laves and Kaldis in Zurich, and Hans Schmid in Geneva. In 1970 the first International Conference on Vapor Growth and Epitaxy was organized by E. Kaldis, myself and others at a time when at least 12 crystal growth laboratories already existed in Switzerland. The first European Conference on Crystal Growth in 1976 was again organized by Kaldis and myself, when I introduced poster sessions for the first time which were then widely accepted. After 1980, short-term profits in industry became dominant so that, unfortunately, most crystal growth laboratories with their long-term developments were terminated.

The industrial production of crystals of silicon, GaAs, InP, SiC, sapphire/ruby, quartz, Li-niobate, CdTe, garnets etc. developed slowly because there had been, and still is, no education of crystal technologists. Companies had to hire a chemist, physicist, or materials engineer and train him for up to 10 years to become an independent crystal producer/engineer working without supervision. Most companies would be happy if they could hire crystal technologists. How much faster could silicon technology have been developed if there had been well-educated crystal technologists?

The problem of educating crystal engineers is multi-disciplinary. It involves, besides crystal growth mechanisms and crystal technology, chemical and materials engineering/thermodynamics, mechanics, including hydrodynamics and aerodynamics, aspects of crystallography and of solid-state physics, machine and process engineering, and of course computer simulation and informatics, of the latter fields the basics so that the crystal technologists can discuss and collaborate (details in WHITE PAPER in Project 16 of the homepage). This education would prevent the application of ten or more different methods to produce silicon solar cells instead of one optimum technology with respect to crystal quality and cell performance, economics, efficiency of process, and ecology. Similar arguments can be applied to laboratory crystal growth for research samples, and to epitaxial deposition processes.



# Understanding the structure-derived function of metal-organic frameworks and their application in separations

Mehrdad Asgari (1), Eric D. Bloch (2), Matthew R. Hudson (3), Craig M. Brown (3), Jeffrey R. Long (2), and Wendy L. Queen (1)

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Currently, separation processes consume an estimated 10-15% of global energy. With this and the expectation that energy consumption will greatly increase with continued population growth and the implementation of large-scale carbon capture efforts, there is intensive scientific focus on the development of new adsorbents. The goal is to design new materials that might enable more energetically favorable separations compared to traditional distillation processes. This feat is not easy, as the differences in the molecules of interest, such as CO<sub>2</sub> and N<sub>2</sub>—the main components in a post combustion flue gas, are minimal. As such, these separations require tailor-made adsorbents with molecule specific chemical interactions on their internal surface.

Metal-organic frameworks (MOFs) have garnered much attention as next generation porous media for various applications, such as small molecule storage and separations. These materials, constructed by metal-ions or metal-ion clusters that are interlinked by organic ligands, offer unprecedented internal surface areas allowing the adsorption of large quantities of guest species. The molecular nature of the organic ligands within the hybrid organic/inorganic newcomers, induces structural versatility, allows the introduction of multifunctional properties, and permits a modular approach to their design. In these ways MOFs, which offer unmatched opportunities to achieve optimal efficiencies in many environmentally relevant applications, are unique relative to their all-inorganic counterparts. New MOFs are regularly reported; however, to develop better materials in a timely manner for specific applications, the interactions between guest molecules and the internal surface of the framework must first be understood. In this presentation, I will provide an introduction to metal-organic frameworks and show our results focused on understanding their structure-derived function. Particular emphasis will be placed on applying *in-situ* x-ray and neutron diffraction techniques to elucidate small-molecule interactions in several families of frameworks. I will also show that through the study of families of MOFs that undergo extensive chemical substitution, one can provide a platform to test the efficacy and accuracy of developing computational methodologies in slightly varying chemical environments, a task that is necessary for their evolution into viable, robust tools for screening large numbers of materials.

# **Energetics of Lattice and Electronic Degrees of Freedom**

Prof. Johan Chang

Laboratory for Quantum Matter Research, University of Zurich

Peierls transitions in one-dimensional systems are perhaps the best-known examples of electronic driven crystal structure transitions. In two dimensions, the problem remains of conceptual interest. This talk will present recent examples of quasi two-dimensional correlated electron systems coupled strongly to the crystal lattice. Three different types of unconventional superconducting systems will be presented and the importance of the lattice symmetry discussed. The last part of the talk, will be devoted to a machine learning approach for recognition of structure factor patterns.

## ***2.Oral contributions***

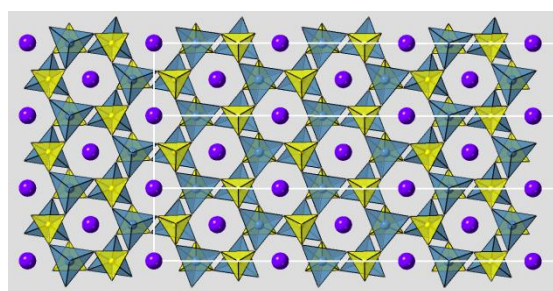
# DFT Calculations of Twin Boundaries in $\text{KLiSO}_4$

Hans Grimmer and Bernard Delley

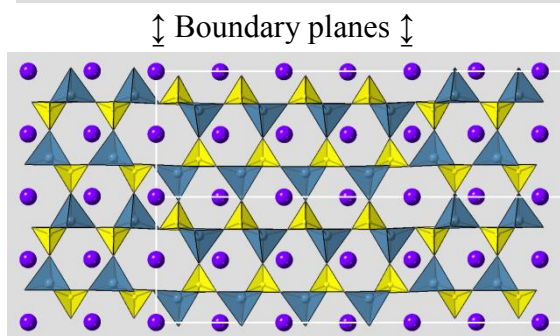
*Paul Scherrer Institut, Research with Neutrons and Muons, 5232 Villigen PSI, Switzerland*

The room temperature phase of  $\text{KLiSO}_4$  has the tetartohedral hexagonal space group  $P6_3$ . It follows that three merohedric twin laws are possible: mirror reflection twins with  $m \parallel [001]$ , rotation twins with  $2 \perp [001]$  and their combination, inversion twins. Structural models for these three laws have been proposed in [1] for boundary plane  $(1\ 0\ \bar{1}\ 0)$ , and, in the case of mirror reflection twins, also for boundary plane  $(0\ 0\ 0\ 1)$ .

The energies of these twins are studied here for the first time. For this purpose, density functional theory calculations have been carried out using the DMol<sup>3</sup> code with the functional PBEsol [2]. Polysynthetic twins with constant lamellae thickness have been considered for thicknesses 1 to 4 times the minimum value that is possible for structural reasons. The energies rapidly converge with increasing lamellae thickness.



*Relaxed inversion twin with boundary planes  $(1\ 0\ \bar{1}\ 0)$  and lamellae thickness four times minimum, viewed parallel and perpendicular to the 6-fold axis of  $\text{KLiSO}_4$*



*O at the edges of the tetrahedra,*

*S inside the yellow tetrahedra*

*Li inside the blue-green tetrahedra*

*K violet balls*

Most common is the mirror reflection twin with boundary plane  $(0001)$ . In this case, the polysynthetic twins have energy 0.001 eV per unit cell independent of lamellae thickness. For maximum lamellae thickness, the energies per unit cell found for the polysynthetic twins with boundary plane  $(1\ 0\ \bar{1}\ 0)$  were 0.09 eV for the inversion twin, 0.55 eV for the rotation twin and 0.58 eV for the mirror reflection twin. The first case was frequently observed in growth twins doped with Cr, the second was never observed and the third only rarely.

[1] H. Klapper, Th. Hahn & S.J. Chung, “*Optical, Pyroelectric and X-ray Topographic Studies of Twin Domains and Twin Boundaries in  $\text{KLiSO}_4$* ”, Acta Cryst. **B43** (1987) 147-159.

[2] B. Delley, “*From molecules to solids with the DMol<sup>3</sup> approach*”, J. Chem. Phys. **113** (2000) 7756-7764.

# Neutron diffraction studies of oxygen disorder in $\text{Nd}_2\text{NiO}_{4+\delta}$

S. Maity<sup>1,2</sup>, J. Schefer<sup>1</sup>, L. Keller<sup>1</sup>, M. Ceretti<sup>3</sup>, W. Paulus<sup>3</sup>

- 1) Laboratory for Neutron Scattering and Imaging, Paul Scherrer Institut, 5232 Villigen, Switzerland.
- 2) University of Geneva, Department of Quantum Matter Physics (DQMP) 24, Quai Ernest Ansermet CH-1211 Genève 4, Switzerland
- 3) Institut Charles Gerhardt, UMR 5253, CNRS-University Montpellier, 34095 Montpellier, France

Better understanding of oxygen diffusion mechanism in non-stoichiometric oxides becomes essential for further development of intermediate temperature solid oxide fuel cells. In this prospect, rare earth nickelates ( $\text{R}_2\text{NiO}_{4+\delta}$ ) emerged as promising materials in which oxygen could be intercalated with electrochemical methods at room temperature. The crystal structure consists of  $\text{RNiO}_3$  perovskite layers sandwiched between  $\text{R}_2\text{O}_2$ -type rock salt layers and extra oxygens are intercalated in tetrahedral sites inside the rock salt layer. Oxygen diffusion, in these materials, is highly anisotropic and described by interstitialcy hopping mechanism [1] at high temperature ( $\approx 800^\circ\text{C}$ ) in which excess oxygens diffuse via apical site inside the rock salt layer. However, close to room temperature, oxygen diffusion is non-Arrhenius type rather a phonon assisted process [2].

In this talk, I will address neutron diffraction studies which were recently performed on powder and single crystal  $\text{Nd}_2\text{NiO}_{4+\delta}$  compounds (with  $\delta=0.25$ ; S1 and 0.1; S2) as a function of temperature to obtain useful insights on phonon assisted diffusion mechanism. Superstructure reflections related to 3d-ordering of excess oxygens were found below 823 K in S1, confirming the pinning of excess oxygens to the crystal lattice and incommensurate crystal structure while the average structure is orthorhombic  $Fmmm$ . Incommensurate oxygen superstructure reflections start to drop intensity around 400 K and loss of 3d-oxygen ordering occurs around 823 K accompanied by  $Fmmm$  to  $F4/mmm$  structural transition. In comparison, the crystal structure of S2 sample is tetragonal commensurate  $P4_2/ncm$  and shows no evidence of long range ordering of excess oxygens in the investigated temperature range. Least square refinements of neutron diffraction data of both samples show unusually high anisotropic thermal displacement factors both for equatorial and apical oxygen atoms showing amplitudes toward [001] and [110] direction respectively *w.r.t.* the  $F$ -symmetry cell, which are getting amplified in the high temperature phase. Maximum entropy reconstruction of neutron data shows additional anharmonic displacement of apical oxygen atoms toward nearest interstitial site due to steric chemical pressure from excess oxygen atoms. We show that such displacement pattern of apical oxygens, largely depends on amount of intercalated oxygen atoms and also reported previously with ab-initio calculations [3] on  $\text{Nd}_2\text{NiO}_{4+\delta}$  compounds, are important pre-requisite for oxygen diffusion close to room temperature.

- [1] Chreneos. A. et.al. J. Mater. Chem., (2010) 20, 266 [2] Ceretti M. et.al. (2015) J. Mater. Chem. A 3, 21140  
[3] Perrichon. A. et. al. (2015) J. Phys. Chem. C 119, 1557

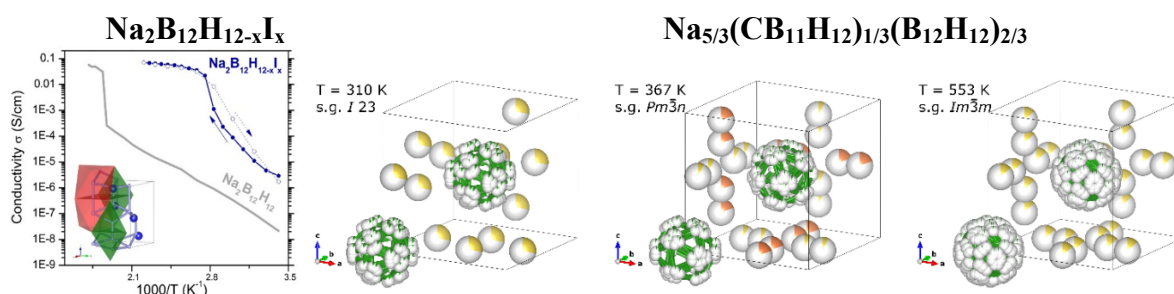
## Metal Hydro-Borates for Li- and Na-ion Batteries

R. Černý, M. Brighi, E. Didelot, Y. Sadikin, F. Murgia, P. Schouwink  
*DQMP, Laboratory of Crystallography, University of Geneva*

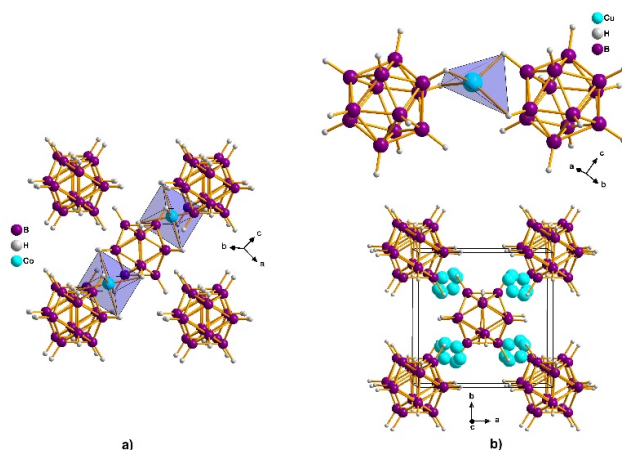
Complex hydrides based on light hydro-borate anions such as borohydride  $\text{BH}_4^-$  or *closo*-borate anion  $\text{B}_{12}\text{H}_{12}^{2-}$  find their place as solid stores for hydrogen, and since recently, also as solid electrolytes in Li- and Na-ion batteries. The mobility of the cations depends on the pathways available in the anion packing, chemical interaction of cations with anions and on the anion thermal motion such as tumbling or rotation. While the latter two require important experimental and theoretical effort, the first parameter can be easily analysed and quantified from the crystal structure data obtained by X-ray diffraction.

Improving  $\text{Na}_2\text{B}_{12}\text{H}_{12}$ , promising Na-ion solid electrolyte, by anion modification and anion mixing will be shown (Figure 1).<sup>1-3</sup> Novel synthetic way completed by *ab initio* structural characterization and *ab initio* calculation allowed discovery of several 3d transition metal *closo*-borates - potentially battery electrodes (Figure 2).<sup>4</sup>

- [1] Sadikin Y., Brighi M., Schouwink P., Černý R., *Adv. Energy Mater.* **2015**, 1501016  
 [2] Sadikin Y., Schouwink P., Brighi M., Łodziana Z., Černý R., *Inorg. Chem.* **2017**, 56, 5006-5016  
 [3] Brighi M., Murgia F., Łodziana Z., Schouwink P., Wolczyk A., Černý R., submitted.  
 [4] Sadikin Y., Didelot E., Łodziana Z., Černý R., *Dalton Trans.* **2018**, 47, 5843-5849



**Figure 1: (left)** Ionic conductivity of a sample containing 52 wt%  $\text{Na}_2\text{B}_{12}\text{H}_{12-12x}\text{I}_x$  and 48 wt% NaI. The conductivity of the precursor  $\text{Na}_2\text{B}_{12}\text{H}_{12}$  is shown for comparison. Na-ion conduction channels in *hcp* sublattice with face-sharing T and O interstices sites in *h*- $\text{Na}_2\text{B}_{12}\text{H}_{12-12x}\text{I}_x$ . In blue the static Na positions as optimized by DFT. **(right)** Evolution of anionic and cationic disorder in  $\text{Na}_{5/3}(\text{CB}_{11}\text{H}_{12})_{1/3}(\text{B}_{12}\text{H}_{12})_{2/3}$ . Green and yellow spheres represent boron and sodium atoms respectively. Orange spheres indicates a different Wyckoff site for Na (only in  $Pm\bar{3}n$ ). The colour partial filling indicates the partial site occupation.



**Figure 2: a)** Crystal structure of anhydrous  $\text{M}(\text{B}_{12}\text{H}_{12})$  for bivalent M (Co, Ni) as optimized by DFT. A part of the trigonal structure ( $R\bar{3}$ ) corresponding to the *bcc* unit cell is shown. **b)** Experimental structure of anhydrous *c*- $\text{Cu}_2(\text{B}_{12}\text{H}_{12})$ . The metal is disordered around a position bridging two *closo*-borates. Local coordination as optimized by DFT is shown above

# Crystallinity and crystallite size determination of recrystallized nanocellulose

Zoltán Balogh-Michels, Jean Buffiere, Marc Borrega, Thomas Geiger, Herbert Sixta, Tanja Zimmermann Antonia Neels

*Empa, Swiss Federal Institute for Materials Science and Technology  
Aalto University, School of Chemical Engineering  
VTT Technical Research Centre of Finland*

Cellulose is a versatile and abundant biopolymer, which is already used in many applications. Nanocellulose, either in the form of cellulose nanofibrils or cellulose nanocrystals has extended these applications in bio-nanocomposites and hybrid functional materials [1].

In this work we are going to present X-ray diffraction investigation of nanocellulose produced by recrystallization of microcrystalline cellulose (MCC) through hydrothermal (HTC) and microfluidic methods (MFC) [2].

The microfluidic treatment did not change the  $\beta$ -I crystalline structure of the microcrystalline cellulose (Fig. 1). The hydrothermal treatment however resulted in a cellulose material which is dominantly  $\beta$ -II. The crystallinity ratio was about 80% for all the MCC, HTC and MFC independently of the estimation method. The crystallite size was determined by the Scherrer-equation. For the MCC and MFC materials the domain size was 7 nm, while a growth to about 12 nm was observed for the HTC material.

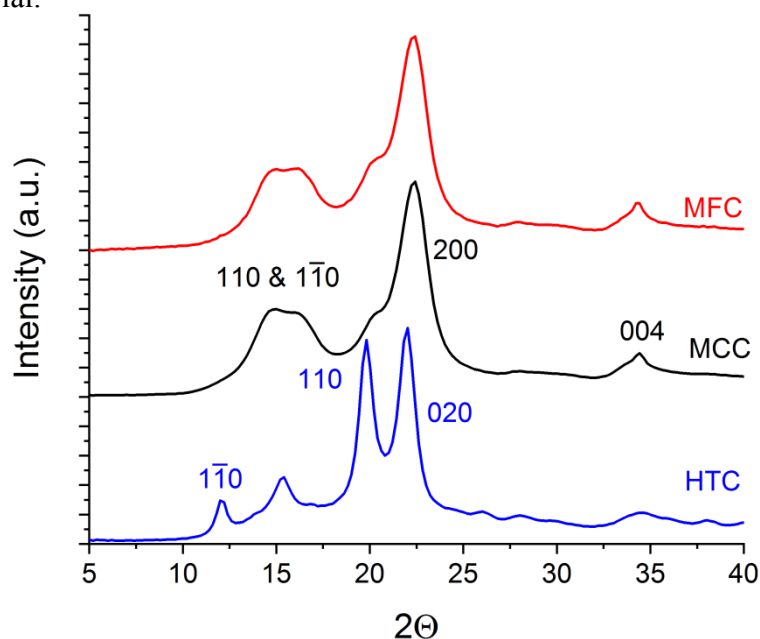


Fig. 1: the XRD spectra of the MCC, MFC and HTC materials, and the peaks of the  $\beta$ -I and  $\beta$ -II cellulose respectively.

[1] T. Abitol et al., Curr. Opin. Biotech., 39 (2016) 76-88.

[2] J. Buffiere et al., Carbohydr. Polym., 178 (2017) 48-56.

## **The Semi-crystalline Structural Features Revealed by Diffractions at Small Angle Regime**

Amin Sadeghpour<sup>1,2,3</sup>, Alex Dommann<sup>1,4</sup>, Antonia Neels<sup>1</sup>

<sup>1</sup>*Empa, Swiss Federal Laboratories for Materials Science and Technology, Center for X-Ray Analytics, Dübendorf, Switzerland*

<sup>2</sup>*Empa, Swiss Federal Laboratories for Materials Science and Technology, Laboratory for Biomimetic membranes and Textiles, St. Gallen, Switzerland*

<sup>3</sup>*Empa, Swiss Federal Laboratories for Materials Science and Technology, Laboratory of Biointerfaces, St. Gallen, Switzerland*

<sup>4</sup>*Cellular and Biomedical Sciences, Faculty of Medicine, University of Bern, Switzerland*

Mesophases are the structures that are neither fully crystalline nor isotropic fluids, but an intermediate state of matter. These thermodynamically stable structures normally form upon self-assembly of molecules in which the building-blocks are partially correlated within a few nanometre range scale. Various macroscopic properties like particular shear viscosity behaviour or their environmental responses are highly dependent to their nanostructures. Detailed understanding of the nanostructural features provides new possibilities for steering the functionality of mesophases, particularly in the field of biomedicine and pharmaceuticals and food science.

At the Center for X-ray Analytics at Empa we are positioned at the intersection of forefront research in materials science towards biomedical applications. The materials include self-assemblies in solution, macromolecules at bio-interfaces and the polymer-based biomimetic membranes for wound dressing. In this contribution, we demonstrate our recent advances in analysis of total scattering at small angle regime from examples of such partially ordered systems. The combined scattering and diffraction signal analysis provides a comprehensive understanding about the multiphase systems. In addition, we will highlight combined small and wide angle scattering approaches to achieve structural characterisation within a wide length-scale.



### ***3. Posters***

## In situ synchrotron scattering studies on ACC colloidal suspension objects in solution

Ahmed S. A. Mohammed, A. Cervellino, A. Testino, A. Carino, M. R. Andalibi

Paul Scherrer Institute (PSI)

The nature of entities present in suspension solutions at the early stage of the precipitation pathway of calcium carbonate is largely debated in literatures. Despite the great scientific relevance of calcium carbonate in different areas of science, little is known about the early stage of its formation. Classical scattering methods such as Wide-Angle X-ray Scattering (WAXS) and Small-Angle X-ray Scattering (SAXS) techniques were employed for the investigations of amorphous calcium carbonate (ACC) entities formed from supersaturated solutions. SAXS, in particular, is important for detecting the entities and investigating their size and shape. SAXS experiments were conducted at the material science beamline (MS – X04SA) of SLS at PSI. We specially designed contactless devices for the measurements, generating liquid jets from supersaturated solution. Four HPLC pumps were delivering diluted solutions (e.g., NaOH, CaCl<sub>2</sub>, NaHCO<sub>3</sub>, H<sub>2</sub>O) in order to obtain a desirable *pH* and saturation (figure 1a). Supersaturation was controlled by mixing four diluted solutions at constant *T* and *pH* and the scattering data were collected using Mythen II detector. The data were modeled using parametric statistical models providing insight about the size and shape distribution of denser matter in the liquid jet. A representative example for the mass distribution of the investigated entities is shown below (figure 1b).

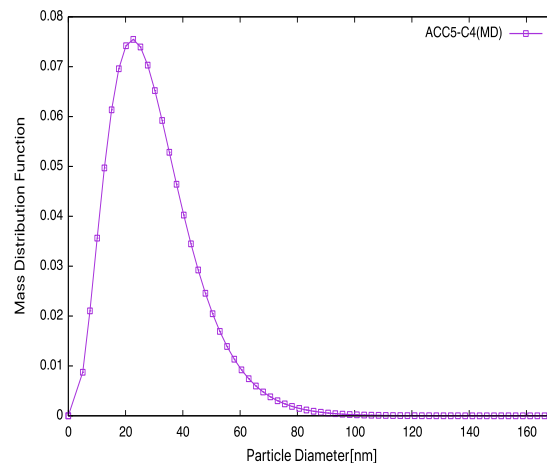


Figure 1. (A) Laboratory setup for generating liquid jets from supersaturated solutions. The solutions are delivered by four HPLC pumps to a mixer and a liquid jet is generated. (B) the mass distribution obtained for one of the supersaturation levels ( $S=1.46$ ).

solutions  
levels (S

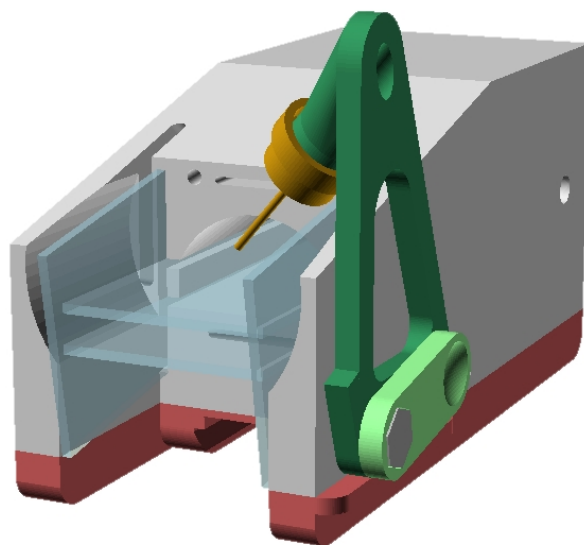
## Low-Cost Portable Devices for Inert Low-Temperature Sample Manipulation

Nils Trapp\*, Michael Solar and Michael Wörle  
Small Molecule Crystallography Center, ETH Zürich, Zürich, Switzerland

Sample cooling has become widely implemented in crystal structure determination, due to the broad array of advantages it offers (Goeta & Howard, 2004). In particular, measurement at reduced temperatures can severely improve data accuracy and resolution for small molecule crystals, due to reduced and more isotropic atomic vibration (Brock & Dunitz, 1990). In addition, it can reduce radiation damage in protein crystals, enable variable temperature or phase transition studies and allow measurements of samples that are not stable or solid under ambient conditions. Low temperature can also prevent crystal damage due to the escape of co-crystallized solvent, which often retains a relatively high vapor pressure. Because the cooling medium used in open-flow sample cryostats is either nitrogen or helium gas, air-sensitive and even pyrophoric crystals can be measured using standard equipment. However, transferring sensitive samples from storage vessel to diffractometer, without compromising crystal and data quality, remains a challenge in many cases.

A straightforward procedure for preparing and mounting crystals under inert conditions is demonstrated, using a specialized apparatus ( $\mu$ CHILL). The technique is extremely flexible, requiring only a single operator, little practice and almost no preparation time. The device enables a wide temperature range (at least  $-60\text{ }^{\circ}\text{C}$  to room temperature), providing temperature control and very stable conditions with no ice formation over extended time periods. The flexible, modular and low-cost design is based on 3D printed parts and readily available standard components, potentially making the device available to a wide range of users and applications not limited to single crystal studies.

### References:



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Goeta, A. E. & Howard, J. A. K. (2004). *Chem. Soc. Rev.* 33, 490–500.  
Brock, C. P. & Dunitz, J. D. (1990). *Acta Cryst. B.* 46, 795–806.

# "NEMS for sensing applications: structural understanding by combining X-ray nano-diffraction and micro-Raman methods"

Simone Dolabella<sup>a\*</sup>, Zuhail Tasdemir<sup>c</sup>, Oliver Braun<sup>a</sup>, Yusuf Leblebici<sup>b</sup>, Erdem Alaça<sup>c</sup>, Gilbert Chahine<sup>d</sup>, Michel Calame<sup>a</sup>, Alex Dommann<sup>a</sup>, Antonia Neels<sup>a</sup>

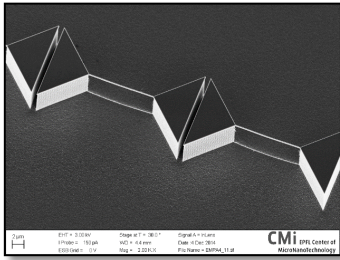
<sup>a</sup> EMPA – Swiss Federal Laboratories for Materials Science and Technology, Dübendorf,

<sup>b</sup> EPFL – Swiss Federal Institute of Technology Lausanne, Switzerland,

<sup>c</sup> Department of Mechanical Engineering, Koç University, Istanbul, Turkey

<sup>d</sup> ID01 X-ray Nanodiffraction beamline, European Synchrotron Radiation Facility, Grenoble, France

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In the last decades the wide field of applications of electronic devices and the miniaturization of materials brought us to study and develop devices such as MEMS and NEMS especially due to the increase in demand from the medical and aerospace sectors. The applicability of Nanoelectromechanical systems (NEMS) is based on their ability to operate reliability over time under service conditions. The purpose is to link atomic structure and physical properties for silicon NEMS. The object under investigation - the nanowire system - is shown in *figure*. A monolithic fabrication has been performed. Structural analysis such as High Resolution X-ray Diffraction (HRXRD) for defect and strain analysis has been applied and performed using the nano-beamline ID01 at the ESRF. HRXRD is used as a non-destructive method to gather more structural information on the inner part of the material framework<sup>[1]</sup>. The performed experiments show us that the intensity of the diffracted X-ray beam of the Si-nanowire can be probed on the given setup. The Y and Z scanning of the shows that the Si-pillars and nanowires exhibit inhomogeneous strain, defect and tilt states. The reciprocal space map (RSM) shows the 2D and 3D diffraction peaks of the substrate and for the Si-nanowires superposed with the Si-pillars. In addition, the use of micro-Raman spectroscopy will support the discussion about local strain<sup>[3]</sup> within the nanowires. These methods are also combined with FEM simulations in order to evaluate diffraction patterns with respect to material parameters such as Poisson's ratio, Young's modulus etc.. This approach allows us to go one step further in understanding mechanical, electrical or thermal behaviors of this class of nanowires.

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[2] Tasdemir Z., Wollschläger N., Österle W., Leblebici Y. and B Erdem Alaca. *Nanotechnology*, 2016, 2, 8.

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**Keywords: silicon nanowires, HRXRD, micro-Raman**

# Effect of shock peening on residual stresses in Selective Laser Melting

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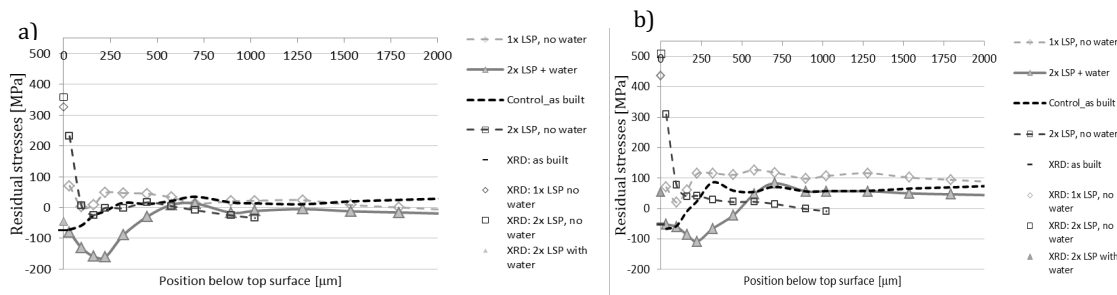
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**Keywords:** Selective Laser Melting, Laser, Shock peening, residual stress, XRD

Selective Laser Melting (SLM) processing of metals results in high residual stresses, that limit the mechanical properties of the fabricated material, which can directly affect the industrial applicability of the process. Laser shock peening (LSP) is a potential technology to engineer such stresses, in order to render them beneficial towards the mechanical stability of the material. This work investigates the influence of overlapping laser shocks and water confinement on the surface microstructure and the related surface residual stress profiles of 316L stainless steel (SS316L). The near-surface stress state was measured using X-Ray Diffraction (XRD) measurements through the  $\sin^2\Psi$  method, measured in four  $\phi$  directions ( $0^\circ$ ,  $45^\circ$ ,  $90^\circ$ ,  $135^\circ$ ). Based on these data, the principal stresses  $\sigma_{11}$  and  $\sigma_{22}$  are calculated. The residual stress state was also measured as a function of depth beneath the SLM- and LSP-treated top surface using the incremental centre-hole drilling (ICHD) technique.

LSP of SLM-processed SS316L without water confinement results in strong tensile residual stresses at the immediate surface of the samples and imparts no beneficial compressive stress state at the surface. On the other hand, LSP of SLM-processed SS316L with a water confinement increases the magnitude and depth of compressive residual stress. Laser peening at  $2.8\text{GWcm}^{-2}$  with dual shocks and 50% overlap, resulted in a maximum compressive stress of  $-200\text{MPa}$ , with the compressive stress state extending down to  $500\mu\text{m}$  beneath the treated surface.

Since the use of water during the SLM build process is not feasible, the possibility of developing a hybrid additive manufacturing build process with in-line LSP will require an alternative solution to water confinement. The results of this study enable process optimisation to open new opportunities in post-processing and hybrid manufacturing of high-quality SLM-parts in combination with laser shock peening.



**Image 1:** a) Minimal and b) maximal principal residual stress profiles for different LSP conditions when compared to the as-built condition. The near surface (at position 0) values are obtained from XRD analyses.

# Pure gyrotropic phase transitions in the arcanite related materials $\text{PbMGeO}_4$ ( $M = \text{Ba}, \text{Sr}$ )

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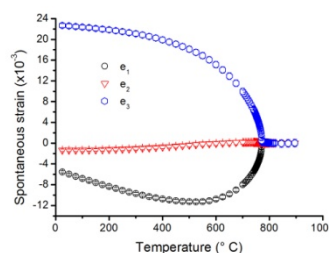
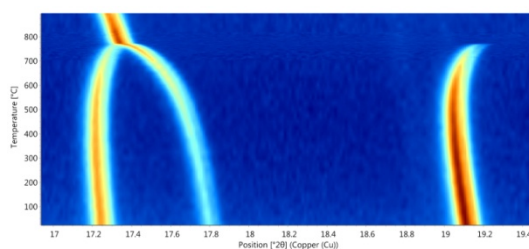
Gyrotropic phase transitions are characterized by the appearance of a spontaneous optical activity [1]. The appearance of such activity is very common in ferroelectric materials. In such materials, the optical activity is a secondary order parameter and is coupled to the primary order parameter which is the electrical polarization. However, only very rare examples are known of a pure gyrotropic phase transition. Among those, one can cite  $\text{BiFeO}_3$  under strain [2] or  $(\text{C}_{2n}\text{H}_{2n+1}\text{NH}_3)_2\text{ZnCl}_4$  as function of temperature [3]. In both cases, the transition exhibits a change from  $\text{Pnma}$  to  $\text{P2}_1\text{2}_1\text{2}_1$  symmetry.

In this contribution, we have investigated 2 materials belonging to the  $\text{BaNdGaO}_4$  structural type, namely  $\text{PbBaGeO}_4$  and  $\text{PbSrGeO}_4$  using powder X-ray diffraction as function of temperature. While  $\text{PbBaGeO}_4$  exhibits a first order phase transition from  $\text{P2}_1\text{2}_1\text{2}_1$  to  $\text{Pnma}$  symmetry,  $\text{PbSrGeO}_4$  exhibits a second order phase transition.

Not only,  $\text{PbBaGeO}_4$  exhibits a first order phase transition but especially show a phase coexistence and competition over a wide range of about  $200^\circ\text{C}$ .  $\text{PbSrGeO}_4$  shows a towards a  $\text{Pnma}$  nearly metrically

This work that both purely

and identify  $\text{BaNdGaO}_4$  structural type as a new source for such materials. Furthermore, those phase transitions seem unusual in light of the complex behavior reported here for these 2 compounds.



temperature  
On the contrary, phase transition structure with hexagonal cell. demonstrates materials are gyrotropic

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**Keywords:** gyrotropic materials, phase transitions, spontaneous strain

# Study the effect of nanofiber fabrication processes into the modification of internal structure at nanoscale

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Electrospinning has been developed as a technique to produce nano to micron-sized fibers. It is well understood that the internal structure of these fibers highly depends on the polymer type, the spinning solution properties and the spinning parameters [1]. In our recent studies, we have investigated the structure of electrospun Poly(vinylidene fluoride-co-hexafluoropropylene), PVDFhfp, based fiber membranes for non-aligned and aligned (using a high speed rotating drum) samples by SAXS and WAXS techniques. We demonstrate that high operational speed of a rotating drum collector used for nanofiber fabrication modify the degree of alignment of the nanofibers without modifying the internal structure of the nanofibers. Furthermore, there is a possibility to modify the internal structures at nanoscale length at extremely high speed of the rotating drum along with the degree of alignment.

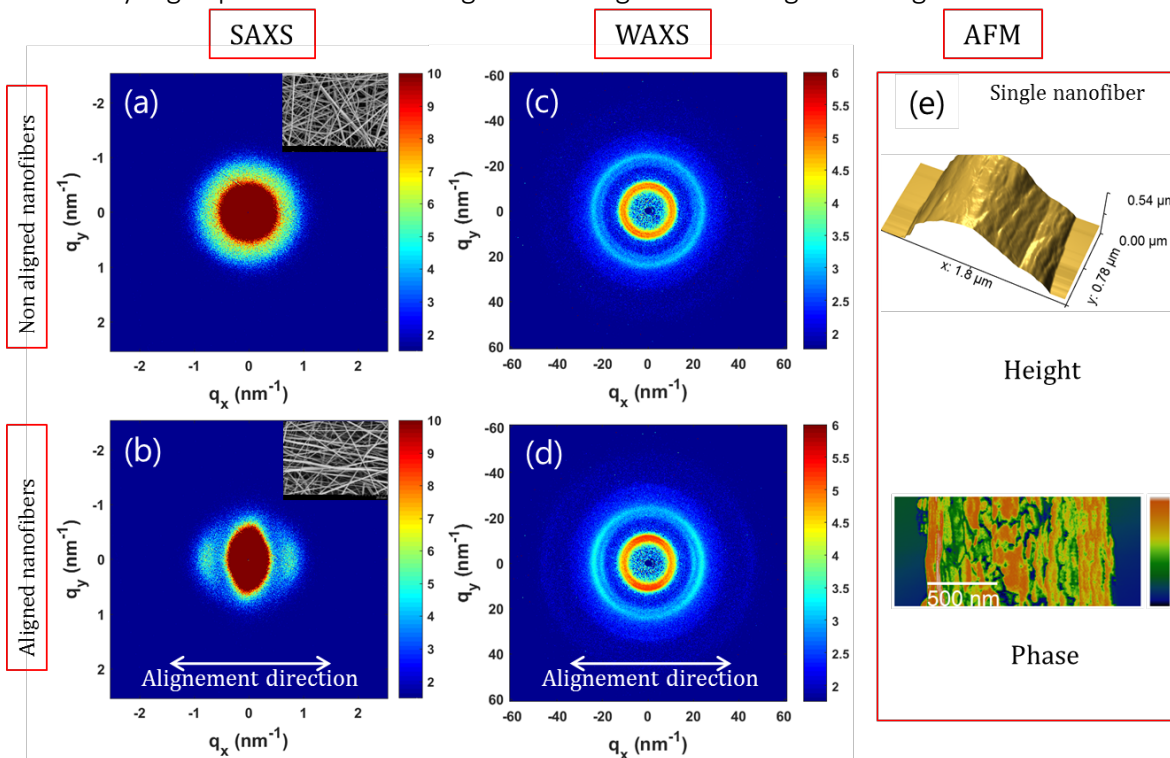


Figure 1. SAXS and WAXS profiles from PVDFhfp fibers; (a,c) non-aligned, (b,d) aligned samples, and their corresponding SEM image in the inset. (e) AFM of single fiber, height (top) and phase image (bottom). [1] D. Kolbuk, P. Sajkiewicz, K. Maniura-Weber, G. Fortunato, *European Polymer Journal*, **2013**, 49 2052.

# **Novel quantitative method based on small angle X-ray scattering for in-situ understanding of nanoparticles agglomeration kinetics**

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## **Abstract:**

Colloidal stability of nanoparticles in biological media is a crucial issue in bio-medical application since the change in the size distribution could change the nanoparticles behavior and cause some undesired effects. An experimental method for in-situ quantitative observation of nanoparticles agglomeration in biological media would provide detailed understanding about the influence of effective parameters at nano-bio interfaces. For biomedical applications, the agglomeration kinetics of nanoparticles at different environments are not concretely determined yet. Here we develop an in-situ method based on small angle X-ray scattering and microfluidics to measure the agglomeration rate constant and the mean agglomeration number of nanoparticles. By using this method, the influence of various buffer systems, ionic strength, pH, temperature, and competing biomolecules such as proteins on nanoparticles agglomeration can be studied. In addition, a comparative analysis by dynamic light scattering (DLS) has been carried out which demonstrates a good agreement with SAXS data.



# Effects of crystallization on electronic and optical properties of SnO<sub>2</sub> transparent conducting oxide thin films

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## Abstract

Intrinsically doped SnO<sub>2</sub> films were grown by sputtering at 60°C in order to study the effects of crystallization upon annealing on electronic and optical properties of the films for applications as transparent conductive electrodes. Post-deposition annealing of as-grown films above 350°C leads to a decrease of charge carrier concentration and mobility. By performing in-situ high-temperature XRD analysis we have demonstrated that this degradation of electrical properties occurs due to formation of grain boundaries and reduction of the donor defect concentration as a result of crystallization of the amorphous as-grown films. Post-deposition annealing has, however, a positive effect on the optical properties of the films. Annealed crystallized samples exhibit lower absorptance in the visible and near-UV wavelength range due to a blue shift of the absorption edge, which results from the decrease of sub-bandgap states associated to point defects. Obtained results indicate that in order to achieve the best combination of electronic and optical properties of SnO<sub>2</sub> films for applications as transparent conductive electrodes the post-processing annealing temperature shall not exceed 350°C at which the films start to crystallize.

## Applications of PDF Analysis to Organic Molecular Compounds

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Total scattering methods have been used for many years to study short-range behaviour in liquids and glasses. The Pair Distribution Function (PDF) methodology gained popularity when nanomaterials became a popular area for study, and continued when local-range effects in inorganic functional materials were recognized as important factors.

The application of the technique to organic molecular systems has traditionally been a more modest area of study but is growing in importance as the use of amorphous materials in pharmaceuticals has grown rapidly. Where structural and quantitative phase analysis using reciprocal space data has become a routine tool for crystalline materials and formulations, PDF may provide some of the same information for nanoscale, amorphous and mixed formulations. The more limited potential information available in a PDF versus a Bragg dataset increases the tendency to over-parameterization and challenges the analyst to become more imaginative with respect to the possible physically and chemically-reasonable restraints and constraints that may be applied.

The study of organic molecular systems via PDF present some additional problems over and above the more familiar systems. The reduced scattering power of the samples means accurate corrections for background, multiple scattering and Compton scattering are increasingly important compared to many semiconductors and oxides for instance. The non-spherical shape of many of the molecules makes  $r$ -dependent corrections for factors such as  $U_{iso}$  less useful than for other systems due to the significant overlap in  $r$  between intra- and inter-molecular interactions. The approach published by Prill *et al* [1] offers a work-around to better fit this troublesome region. Amorphous materials become even more problematic with truncation of small angle scattering and an uncertain shape function among the issues that may become apparent. Extracting information about the intermolecular interactions in an amorphous system ideally requires stripping out the single molecule contribution to the reduced PDF. Benmore *et al* [2] fitted  $S(Q)$  in the high  $Q$  region to extract the single molecule  $U_{iso}$  to more accurately model the single-molecule peak widths in the  $G(r)$ .

Examples will be given highlighting some of the problems that may be encountered, current approaches that may be used to overcome them, and where further developments may be required to fully realize the technique's potential.

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**Keywords:** PDF, molecular systems, pharmaceuticals

# Formation of hybrid organic-inorganic guanidinium lead(II) iodides from mechanochemical reactions

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Mechanochemistry is increasingly used for solid state reactions because of its advantages like high yields, high conversion rates, the easy handling, the small produce of waste and the good energy consumption, for which it belongs to green chemistry.<sup>1-3</sup> Metal organic frameworks and cocrystals are the most studied materials. Nevertheless, the mechanisms behind mechanochemical reactions are still under investigation. Recently, setups were developed for monitoring mechanochemical reactions *in situ* using X-ray diffraction<sup>4</sup>, Raman spectroscopy<sup>5</sup> or both combined.<sup>6</sup> In all setups the originally steel made milling jar is replaced by a plastic jar.

Here we present the *in situ* investigation of the formation of a series of organic-inorganic hybrid materials from mechanochemical synthesis. The compounds are constructed by guanidinium-, lead(II)- and iodide-ions, with the formula  $(C(NH_2)_3)_nPbI_{2+n}$ . For the *in situ* investigations a new setup, developed at the MS beamline is used.<sup>7</sup> Due to the gained high quality data an automatic quantitative analyses of the time-resolved powder patterns was possible and revealed intermediate formations, solid-solid phase transitions and reactions between the guanidinium lead(II) iodides during the syntheses.

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## **Mesquik, a mail-in service for synchrotron powder diffraction at SLS**

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Paul Scherrer Institute

The Material Science beamline at the SLS offers different types of diffraction experiments to its users via an external-review proposal system.<sup>1</sup> A faster access proposal system for powder diffraction, named Mesquik, is also in place. It consists of a permanently-open, fast-tracked and externally-reviewed system for simple powder diffraction data collections. It provides for accepted proposals synchrotron data delivered to a mailbox within 10 weeks from the proposal submission. The limitations and characteristics of the service will be presented, including general guidelines on how to plan its usage.

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<sup>1</sup> <https://www.psi.ch/sls/ms/pd-mesquik>

# Total Scattering at the X04SA beamline of SLS

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The X04SA Powder Diffraction beamline [1] has been developed with Total Scattering (TS) experiments at the forefront. The requirements for TS are perfectly compatible with maintaining the best capabilities for classical synchrotron XRPD, as the main TS requirement is – top data quality. The energy flexibility of the beamline (5 – 30 keV with high photon flux and sufficient detection efficiency) and the excellent detectors installed (a 2D Pilatus 6M and a large 1-D Mythen II) make up the rest, allowing for the required momentum transfer especially with the Mythen II [1]. In fact, collecting data to 140 deg with the Mythen, the  $Q_{\max}$  can reach  $> 28 \text{ \AA}^{-1}$ , sufficient for most materials, while especial emphasis is given to reciprocal space TS (modelling the data directly from atomic coordinates via the Debye Scattering Equation, as per the DFA method [2]), where the absence of a direct Fourier transform of the data makes the need for high  $Q_{\max}$  less stringent whilst the data quality must be even higher in all respects. Increasing data quality is a process that involves the hardware – whereas all forms of parasitic scattering and all instrumental and intrinsic distortions (inelastic scattering, absorption,...) can be minimised and/or corrected whilst maximizing the sample scattering signal. The software plays also a critical role, inasmuch the information content of the data is fully preserved and the raw data are processed, corrected and subtracted [2] to yield precisely the desired part – the sample's elastic scattering pattern and its absolute scale sharpened counterpart  $S(Q)$  or the latter's direct space Fourier equivalent interatomic distance pair distribution function  $G(r)$ . The hardware (rotating capillary, liquid jet and suspended droplet) enhancements will be presented, together with the state-of-the-art, never before presented procedures and algorithms for calibrating the detector (pixel-wise positional and efficiency corrections [2]) together with the most effective and still partly unpublished algorithms and methods for data processing, merging, subtraction and correction – including a novel lossless smoothing-denoising [2] that permits to acquire high-quality low-noise background patterns in a fraction of the time previously required. Furthermore, subsequent processing [2] to obtain the absolute scale sharpened  $S(Q)$  and the  $G(r)$  functions in a reliable and automated way are presented and compared with existing dedicated softwares like GudrunX [3], PdfGetX3 [3]. As an outlook, simultaneous Quantitative Phase Analysis in  $Q$  and  $r$  spaces – thus made independent from the crystallinity of components – is envisaged.

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**Keywords:** Synchrotron XRPD, Total Scattering, Data processing

## BONDING IN POLYIODIDES UNDER HIGH PRESSURE

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High-pressure structures of tetraethylammonium diiodide triiodide (TEAI) were determined in the range up to 12 GPa. Electrophilic  $I_2$  and nucleophilic  $I_3^-$  moieties significantly approach as a function of pressure. This eventually leads to the formation of pentaiodide units at 6.8 GPa, heptaiodides at 7.6 GPa and infinite inorganic polymeric chain at 11.9 GPa. This catenation is anticipated by single crystal- single crystal phase transition at about 5.7 GPa, reducing the lattice symmetry from orthorhombic to monoclinic. The process is reversible, though with a large hysteresis (transition back to orthorhombic system occurs at 1.5 GPa).

Iodine atoms form a zig-zag pattern where neutral iodines act as linkers between triiodide units. Intermolecular interactions between donor and acceptor are asymmetric. Formed higher polyiodide anions repulse each other increasing the distance, whilst they get closer to electrophilic  $I_2$  on the opposite side of the iodine-chain block. Eventually, high pressure drives units as long as heptaiodides to react with each other, forming two-dimensional net at 11.9 GPa. Formation of such a net is anticipated by a high-pressure electrical conductivity measurements. Polymerization of iodine subunits leads to dramatic increase in the crystal conductivity. The nature of iodine-iodine bonds, stabilized under pressure, is investigated by comparing features observed in ambient pressure polyiodides.

There are no unique criteria for what is to be considered a bond. We used the energy decomposition analysis (EDA ) and the interacting quantum atom (IQA) approach together with other criteria such as the delocalization index, the Laplacian of the electron density, or the energy density to clarify the bonding situation. Additionally, orbitals obtained from X-ray constraint wavefunction calculations were analysed in order to better understand the interactions that lead to the bond formation.

# Direct observation of negative thermal expansion in a lanthanide-based metal–organic framework: the impact of framework flexibility and host–guest interactions

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**Abstract.** Materials exhibiting negative thermal expansion are of great interest due to their potential in numerous technological applications. **SION-2**, a lanthanide based metal–organic framework with a formula of  $[\text{Tb}_2(\text{DHBDC})_3(\text{DMF})_4] \cdot 2\text{DMF}$ , displays a highly anisotropic thermal expansion in the 100–340 K temperature range with the linear thermal expansion coefficient of  $-153(6) \text{ MK}^{-1}$  along one out of three principal axes. Through variable-temperature single-crystal X-ray diffraction, it is observed that the intrinsic framework flexibility in combination with the host framework–guest DMF interactions are the key factors responsible for this anomalous thermal behaviour.