



2011 Meeting of the Swiss Crystallographic Association

Abstracts and Program

The annual meeting of the SGK/SSCr and general assembly will take place at Department of Chemistry and Biochemistry, **University of Bern, Freiestrasse 3**, Bern on **Friday September 16, 2011**. The meeting is jointly organized by the groups of Mineralogical Crystallography (Prof. Dr. T. Armbruster) and Chemical Crystallography (PD Dr. P. Macchi) of the University of Bern.

A social dinner (Haus der Universität, <http://www.hausderuniversitaet.ch/>) is scheduled on Thursday September 15, 2011, 19h (evening before the meeting).

More details on the website: <http://www.sgk2011.unibe.ch>

Way from the SBB main station (15 minutes walk):



Registration (meeting and dinner): September 1, 2011

The meeting is free of charge (except for dinner and accommodation).

Meeting Title: **Modern crystallographic techniques for new materials
Program
Scientific Program (16 September, room UG113)**

9.00-10.00		registration /Poster session
10.00-10.05		Welcome message
10.05-10.50*	IT1	Roland Miletich (University of Wien): "Single-crystal diffraction at extreme conditions: Innovative techniques and new trends"
10.50-11.15		Coffee break /Poster
11.15-11.40*	O1	Session 1 (Inorganic materials and minerals) Pascal Schouwink: "Exciting Crystal Chemistry of Bimetallic Borohydrides"
11.40-12.05*	O2	Ravi Sura: "Oxygen Ion Diffusion in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4\pm\delta}$ Investigated by Oxygen Isotope Back Exchange and Diffraction Methods"
12.05-12.30*	O3	Volodymyr Svitlyk: "Influence of temperature and pressure on the crystal structure of the $\text{A}_x(\text{Fe}_{1-y}\text{Se})_2$ ($\text{A} = \text{Cs}, \text{Rb}, \text{K}$) superconductors"
12.30-13.15		Lunch/Poster
13.15-13.45		General Assembly of the SGK
13.45-14.00		Coffee break /Poster
14.00-14.50	IT2	Dylan Jayatilaka (University of Western Australia): "Charge density refinement of X-ray diffraction data without the multipole model: what else can we squeeze out of the data?"
14.50-15.00		Poster Prize Winners announcement
15.00-15.25*	O4	Modeling structure and Properties of materials Riccarda Caputo: "Ab-initio crystal structure prediction"
15.25-15.50*	O5	Anna Krawczuk-Pantula: "Atomic polarizabilities and multipolar model"
15.50-16.15*	O6	Bernard Spingler: "Some thoughts about the single crystal growth of small molecules"
16.15-16.45		Coffee Break/Poster
16.45-17.15*	O7	Facilities and new instruments Dmitry Chernyshov: "3D Mapping of Reciprocal Space with Synchrotron Light "
17.15-17.35*	O8	Olha Sereda: "High Temperature in-situ XRD Studies on New Solder Materials for MEMS Packaging Applications"
17.35-17.55*	O9	Eric Hovestreydt: " Latest Results from CMOS detector technology"
17.55-18.00		Closing Ceremony

* includes 5 minutes for discussion

List of Posters:

- P01 Precursors for oxide materials
- P02 Precursors for ion conducting battery oxide materials
- P03 Optimizing the input parameters for powder charge flipping
- P04 Behaviour of the ring silicate Benitoite $\text{BaTiSi}_3\text{O}_9$ at high pressure
- P05 Crystal structure of the uranyl mineral grimselite, $(\text{K}_{2.43}\text{Na}_{0.57})_{\Sigma 3.00}\text{Na}[(\text{UO}_2)(\text{CO}_3)_3](\text{H}_2\text{O})$, from Jáchymov, Czech Republic
- P06 Crystal structures and microstructures of ordered and disordered kalsilites. Is kaliophilite a KAlSiO_4 polymorph or kalsilite polytype?
- P07 Vibrational (FT-IR and Raman) spectral studies, geometrical parameters and theoretical calculations of triethylenetetramine and its cyano-bridged heteronuclear polymeric complex
- P08 Hetero-metallic coordination polymers: Crystal structures of $\text{trans-}[M(\text{N-Meim})_2\text{Ni}(\square-\text{CN})_4]_n$ ($M=\text{Cu(II)}, \text{Zn(II)}$ and Cd(II))
- P09 Structure analysis of two open-framework zirconium phosphate materials
- P10 The effect of hydration and strain on ceramic proton conductors
- P11 Perfect epitaxial growth of germanium on silicon and crystal quality Quantification by high-resolution X-ray diffraction
- P12 Stepwise in situ dehydration of yugawaralite: a temperature dependent single-crystal X-ray study
- P13 Spin density distribution of the orbital singlet Mn(II) : A polarised and non-polarised neutron diffraction study of the $[\text{Mn}(\text{Imz})_6]_2+(\text{NO}^{3-})_2$ complex, where $\text{Imz} = \text{Imidazole}$
- P14 Intercluster Compounds for Nanosized Materials
- P15 High pressure structure of $\text{Mn}_2(\text{CO})_{10}$: an off-axis M-M bond
- P16 On the purity of multi-layer focused X-ray radiation
- P17 Properties of metal oxalate materials from electron density. Modelling the building blocks and Pd evaluation of framework interaction
- P18 Pavlovskyite $\text{Ca}_8(\text{SiO}_4)_2(\text{Si}_3\text{O}_{10})$ - a new mineral of altered silicate-carbonate xenoliths from the two Russian type localities: Birkhin massif, Baikal lake area and upper chegem caldera, northern Caucasus
- P19 Lithium self-diffusion in $\text{LiAlSi}_2\text{O}_6$ glass and single crystals
- P20 Diffuse scattering study of β -pigment red 170
- P21 α - $''\text{NaLuF}_4''$: 6 fold twinning with modulation and diffuse scattering
- P22 Synthesis of new silver compounds with nicotinic acid derivatives

Abstract Talks

IT1: Single-crystal diffraction at extreme conditions -
Innovative techniques and new trends

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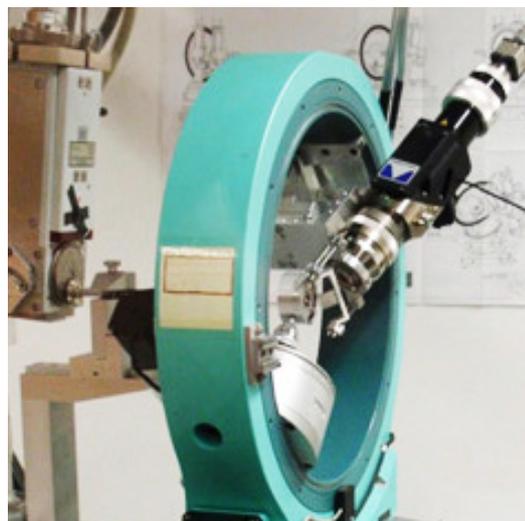
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The demand for obtaining knowledge on the structure-property relationships and hence the crystallography of solids at even more and more extreme conditions has led to a continuous development in techniques applied to in-situ studies at non-ambient sample environments. In order to achieve even more extreme conditions it inevitably involves scaling down available sample sizes and thus giving a renaissance to single-crystal techniques. In particular modern high-pressure research nowadays aims for the multi-megabar pressure regime or the combination of variable pressure settings at e.g. high/low temperatures, electric/magnetic fields, or the sample being simultaneously exposed to any kind of irradiation.

Apart from persistent improvements on the sample environment [1], in particular new heating techniques such as mobile laser-systems [2] (see Fig.) or heatable gaskets [3], new diffractometer components and available sources allow higher resolutions in reciprocal space, a higher sensitivity for faint features (e.g. weak superstructure reflections), and the measurement on shorter time scales. Moreover, time-optimized experiments now allow to retrieve structural information even from samples, which are instable over time. Several examples of recent measurements on various phases will be provided in order to demonstrate the quality from state-of-the-art experimental setups and the current limitations with available techniques.



High-pressure diamond-anvil cell and the mobile laserhead optics mounted on the χ -circle of the Huber four-circle diffractometer in Vienna

- [1] T. Pippinger, R. Miletich, M. Burchard, Rev. Sci. Instrum. (in press)
- [2] L. Dubrovinsky, K. Glazyrin, C. McCammon, O. Narygina, E. Greenberg, S. Übelhack, A.I. Chumakov, S. Pascarelli, V. Prakapenka, J. Bock, N. Dubrovinskaia, J. Synchr. Rad. **16**, (2009)
- [3] R. Miletich, D. Cinato, S. Johäntgen, High Press. Res. **29**, 290 (2009)

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The fascinating diversity in the Crystal Chemistry of novel compounds based on the BH_4^- group continues to proliferate. In this study we contribute with the structural characterization and classification of recently found novel ternary borohydrides, e.g. $\text{K}_2\text{M}(\text{BH}_4)_4$ ($M=\text{Mn}, \text{Mg}, \text{Zn}$) or $\text{KZn}(\text{BH}_4)_3$, based on bivalent Metals, which are brought into a crystal-chemical context and discussed in terms of possible differences concerning the bonding scheme. Currently planned studies on high-pressure polymorphs will also be presented. The examination of the present results is in good agreement with the established and ongoing trend of this compound group to form ionic as well as framework structures closely related to sulfates and oxides as well as halides in general, as observed in numerous recent works. It is shown by Synchrotron Powder Diffraction, backed up by spectroscopical methods, that structural similarities, e.g. between Mn- and Mg-modifications observed for binary borohydrides^[1,2] can be extended to corresponding ternary compounds. The compounds reported here all follow very similar building principles, the most prominent structural unit being isolated complex anions $[\text{M}(\text{BH}_4)_4]^{2-}$ or $[\text{Zn}(\text{BH}_4)_3]^-$, which are charge-compensated by the larger alkaline cation, resulting in packed structures derived from the Sulfates and Halides. Thus, while evidence for the covalent bonding contribution in the binary compounds of the respective M metal lies intrinsically in the connectivity of their distinct frameworks, the big complex anion in the ternary ones has various bonding-schemes as a consequence; the interaction between ligands and the central atom of $[\text{M}(\text{BH}_4)_x]^{n-}$ being of partially covalent character, as deduced by the directionality of hydrogen bonding reported in many works as well as the integrity of the tetrahedron, while on a larger scale the compound crystallizes in well known ionic structure types and their distorted derivatives. The ongoing reports of such structural similarities, culminating in solid solutions, not only extends the promising prospects concerning the precise compositional and structural tunability of this compound class regarding their hydrogen storage properties, but also is a clear hint of structural flexibility with regard to the more complex quaternary structures, which may show greater dependency on structural parameters such as site mixing and occupancies with respect to their physical properties, e.g. Li^+ conductivity.

[1] Ya. Filinchuk, R. Cerny, H. Hagemann, Chem. Mater, **21**, 925 (2009)

[2] R. Cerny, N. Penin, H. Hagemann, Ya. Filinchuk, J. Phys Chem. C, **113**, 9003 (2009)

O2: Oxygen ion diffusion in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4\pm\delta}$ investigated by oxygen isotope back exchange and diffraction methods

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The understanding of oxygen ion conduction in solids at moderate temperatures is a key issue for the development of oxygen membranes in solid oxide fuel cells (SOFCs) [1-3]. The oxygen diffusion in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4-\delta}$ can be decreased by Sr doping as reported by Opila [4]. Sr doping can therefore be used to investigate deeper how

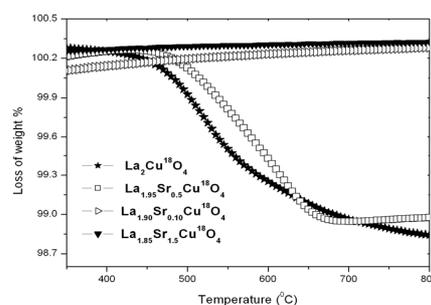
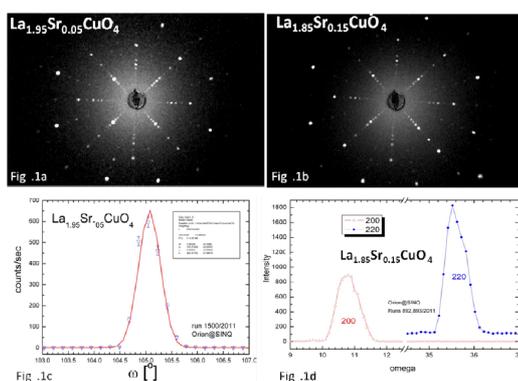


Figure 1a, 1b: Back scattering Laue pictures of as grown single crystals. **Figure 1c, 1d:** High quality single crystal of $\text{La}_{1.95}\text{Sr}_{0.05}\text{CuO}_4$ and (200), (220) collected at ORION@SINQ.

Figure 2. Oxygen Isotope Back Exchange (OIBE) in $\text{La}_{2-x}\text{Sr}_x\text{CuO}_4$ showing the suppression of oxygen diffusion for high Sr doping (x).

diffusion and structure correlate. For this we need to examine high quality single crystal to avoid porosity and grain boundaries present in polycrystalline samples and influencing therefore the equilibrium. We have succeeded to grow $\text{La}_{2-x}\text{Sr}_x\text{CuO}_{4\pm\delta}$ single grain crystals by using a mirror furnace and tested them with X-ray Laue (Fig. 1a, 1b) and neutron diffraction (Fig. 1c, 1d). We did Oxygen Isotope Back Exchange (OIBE) experiments (Fig 2) between 40 °C to 1000 °C we proved that free oxygen mobility can be realized for $x = 0, 0.05$ already below 500 °C but is depressed for $x = 0.10$ and 0.15 . This gives evidence that low temperature oxygen mobility relies on Sr doping in La_2CuO_4 .

[1] Y. Tsujimoto et al., Nature **450**, 1062-1066 (2007)
 [2] A. Villesuzanne et al., J. Solid State Electrochem. **15**, 357-366 (2011)
 [3] L. Le Dréau, Thesis, accepted July 2011 (University of Rennes/PSI)
 [4] E.J. Opila, J. Am. Ceram. Soc. **6**, 2363(1995)

O3: Influence of temperature and pressure on the crystal structure of the $A_x(\text{Fe}_{1-y}\text{Se})_2$ ($A = \text{Cs, Rb, K}$) superconductors

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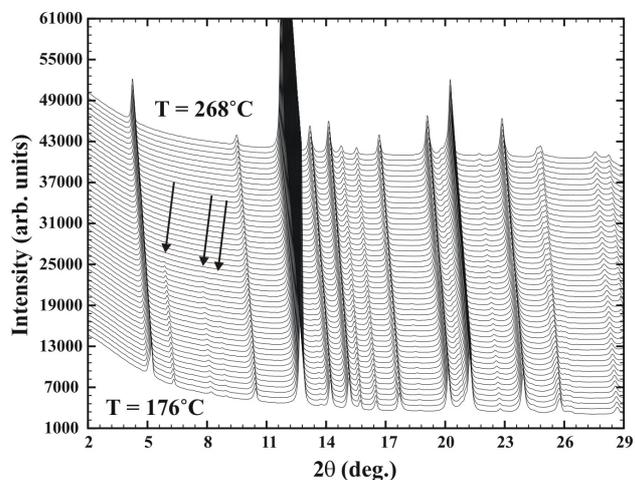
Synchrotron radiation was used to study temperature ($\text{Cs}_x(\text{Fe}_{1-y}\text{Se})_2$) and pressure ($\text{Cs}_x(\text{Fe}_{1-y}\text{Se})_2$, $\text{Rb}_x(\text{Fe}_{1-y}\text{Se})_2$ and $\text{K}_x(\text{Fe}_{1-y}\text{Se})_2$) evolution of crystal structures of the new layered Fe-based superconductors.

$\text{Cs}_{0.83}(\text{Fe}_{0.86}\text{Se})_2$ undergoes a first-order structural transformation on heating associated with the disorder of the iron vacancies in the FeSe layer, as we have shown before [1] and in agreement with

other reports [2]. Irreversibility of the temperature dependence of the lattice dimensions and Bragg intensities is most probably related to a mobility of the intercalated alkali ions. First order of the transition is manifested by the hysteresis in the lattice behavior and also confirmed by the differential scanning calorimetry [1].

No clear pressure-dependent anomalies for $\text{Cs}_{0.83}(\text{Fe}_{1-y}\text{Se})_2$, $\text{Rb}_{0.85}(\text{Fe}_{1-y}\text{Se})_2$ and $\text{K}_{0.8}(\text{Fe}_{1-y}\text{Se})_2$ ($y \sim 0.14$) were observed around 80 kbar, where transport experiments indicate an offset of superconductivity [3]. The Bragg reflections indicative of the vacancies ordering in the FeSe layer do not disappear up to applied pressures of ~ 120 kbar. This indicates that the ordering of the vacancies in the FeSe layer may be present in both superconducting and non-superconducting states.

Thermal expansion coefficients calculated from the temperature dependent diffraction and bulk moduli obtained from the pressure dependent diffraction may serve as constrains for theoretical models.



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[2] W. Bao, G. N. Li, Q. Huang, G. F. Chen, J. B. He, M. A. Green, Y. Qiu, D. M. Wang, J.L. Luo, *arXiv:1102.3674v1*, 2011.
[3] G. Seyfarth, D. Jaccard, P. Pedrazzini, A. Krzton-Maziopa, E. Pomjakushina, K. Conder, Z. Shermadini, *Solid State Commun.* 2011, 151, 747.

IT2	Charge density refinement of X-ray diffraction data without the multipole model: what else can we squeeze out of the data?
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The philosophy and practice of deriving a reasonable single-determinant wavefunction from experimental charge density X-ray diffraction data will be reviewed.

This hybrid "experimental" wavefunction can be used to produce many properties not normally associated with the X-ray charge density technique; for example, electron localization functions (ELF) and Roby bond indices. The message here is that charge density measurements can be used to do far more.

As well as improved qualitative chemical information, results from these "experimental" wavefunctions are presented for some linear and non-linear optical (NLO) properties, namely refractive indices and second order NLO coefficients.

The results from the "experimental" wavefunctions are in better agreement with experimental measurements than those from wavefunctions where no X-ray data is used as input. They are also in better agreement with multi-determinant wavefunction calculations.

As further evidence of the usefulness of wavefunctions which incorporate experimental data, results for geometrical parameters and ADPs for a small dipeptide gly-ala will be presented and compared with corresponding neutron data.

The agreement between such measurements, particularly for hydrogen atoms, has been previously thought to be unachievable from X-ray diffraction data alone.

O4: Ab-initio crystal structure prediction

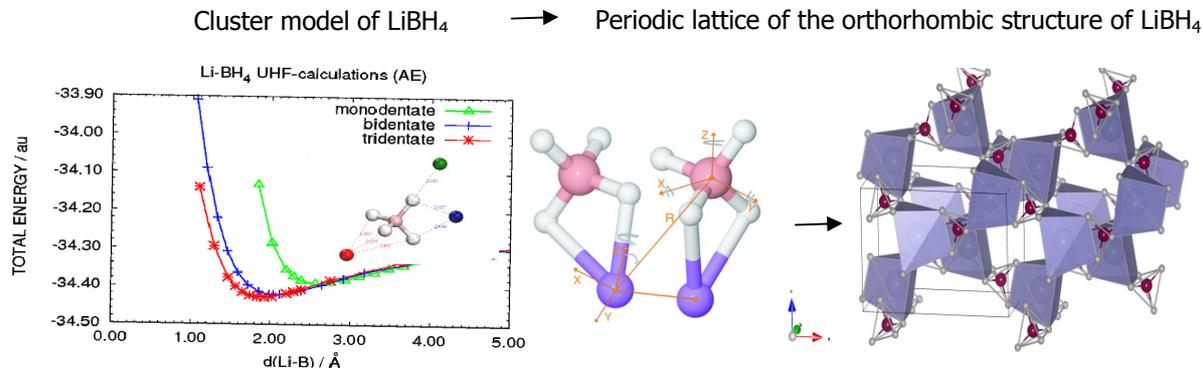
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Ab-initio crystal structure prediction is still one of the most challenging and interesting issue in condensed matter science. The first difficult task is the determination of the irreducible descriptors required to search for the global minima among different conformational geometries, a molecular system can adopt when visiting the many local minima of the potential energy surface.

By presenting some case studies, it will be discussed an ab-initio computational methodology of crystal structure modeling, which combines cluster modeling, via global minimization techniques, and periodic lattice calculations, based on Density Functional Theory. Whereas known experimental structure are available, the comparison with them helps to validate the predictability power of the computational approach and provides a molecular insight of stable and metastable structures of the particular system under study. The examples are represented by the first-principles ground-state structure determination of selected complex borohydrides, metal borides and transition metal oxides of interest in materials science for energy applications.



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- [3] Phys. Rev. Lett. **104**, 215501 (2010)
- [4] Mol. Phys. **108**, 1263 (2010)
- [5] Inorg. Chem. **49**, 8756 (2010)
- [6] J. Solid State Chem. **184**, 1622 (2011)

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When a molecule is placed in an external electric field, its electron distribution changes in response. A useful measure of this effect is the molecular dipole moment together with its first and second derivatives (polarizability, hyperpolarizability). Using the QTAIM theory [1] it is possible to decompose the dipole moments and the polarizabilities into the atomic components. It was previously discussed [2] that each atomic contribution can be expressed as the sum of "atomic polarization" and "charge transfer" contributions. The transfer contribution is given by the weighted translation vector from atom's nucleus to the corresponding BCP, its sign and value strongly depend on the nature and number of bonded groups to the selected atom.

Here we present the relationship between the charge density distribution, obtained with the use of multipole model of Hansen and Coppens [3], and electric properties such as electric dipole moment, as well as the response of a molecule to the external electric field in simple organic molecules. It is well established that the multipolar reconstructed electron density (XD2006 [4]) can provide sufficiently accurate electric moments of a molecule in the crystal, however our results show that this does not hold for derivatives of the electric moments. In particular, while the bond polarity term is sufficiently well reconstructed (at least at zero field), the atomic polarization term is more problematic, even without the application of an external electric field. Empirical methods to estimate the polarizability based on the zero field electron density distribution will be tested, in order to allow estimation of linear optic properties from a multipolar model.

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- [2] T.A. Keith, *Atomic Response Properties in The Quantum Theory of Atoms in Molecules: From Solid State to DNA and Drug Design* C.F. Matta, R.J. Boyd, Eds., Wiley-VCH, Weinheim (2007)
- [3] N.K. Hansen, P. Coppens, *Acta Crystallogr.* **A34**, 909-921 (1978)
- [4] A. Volkov, P. Macchi, L.J. Farrugia, C. Gatti, P. Mallinson, T. Richter, T. Koritsanszky, *XD2006: A computer Program Package for Multipole Refinement, Topological Analysis of Charge Densities and Evaluation of Intermolecular Energies from Experimental and Theoretical Structure Factors* (2006)

O6: Some thoughts about the single crystal growth of small molecules

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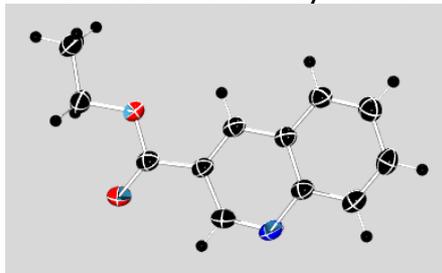
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Crystallisation of suitable single crystals undoubtedly is the most decisive step of a successful X-ray structure determination. Quite often, only an X-ray analysis will definitively reveal the composition and three-dimensional arrangement of an unknown compound. However, this powerful technique fully relies upon the ability to grow single crystals of sufficient quality and size. Although crystallisation is an important purification technique which is taught and widely used in every Chemistry undergraduate curriculum, different techniques may have to be employed for the growth of diffraction-quality single crystals.

One of the useful descriptions about growing single crystals is that of Jones.[1] Kroon and co-worker have summarized the different techniques for growing crystals of organic molecules, though their methods can be extended to many small molecules.[2] Hulliger has described in great detail techniques that are suitable for various types of compounds.[3] On the internet, many pages are dedicated to the description of how to grow single crystals [4, 5]. The crystallisation of active pharmaceutical ingredients has been reviewed.[6] Not surprisingly, several publications have studied the influence of solvents upon the crystallisation of polymorphs.[7, 8] Of course, the use of different solvents often results in solvate crystals as shown for organic crystals[9], metal complexes[10], or pharmaceuticals.[11-13] Since the number of possible solvents is very large, solvents were grouped after statistical analysis of selected solvent parameters.[14-16] However, the knowledge gained from these investigations was not used to tackle an open crystallisation challenge.

Nevertheless, it has been our experience in the last fifteen years, that beginners are often lacking the knowledge of how to setup crystallisation trials. Secondly, even experienced researchers are grateful for hints how to optimize crystallisation setups that hitherto have failed to produce suitable single crystals. We have assumed for the following studies that the compound of interest is available in small amounts of not more than 50 milligrams only. This quite common situation has severe consequences: a quantitative determination of the solubility in common solvents is not possible. Furthermore, some crystallisation techniques cannot be used, because they require more material and they do not allow the recovery of the compound of interest.



The presentation has a two-fold aim: For beginners in the field of single crystal growth, we want to describe and critically compare the most commonly used basic techniques for the growth of single crystals: a) vapour diffusion (including solvent evaporation) and b) solvent layering. We briefly also discuss the unconventional technique of crystal growth in gels. At the same time, we want to give the more advanced

researchers some ideas, in case their standard methods fail to work. In particular, we will show that a careful screening of the solvents, including some uncommon ones, increases the chances of getting single crystals. This is demonstrated by the example of

3-carbethoxyquinoline (**1**, see ORTEP representation of one out of two molecules in the asymmetric unit). In addition, we will share our experience about various aspects of crystallisation that we have accumulated over the last fifteen years.

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- [2] P. van der Sluis, A. M. F. Hezemans, J. Kroon, *J. Appl. Cryst.* **22**, 340 (1989)
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- [7] N. Blagden, R. J. Davey, H. F. Lieberman, L. Williams, R. Payne, R. Roberts, R. Rowe, R. Docherty, *J. Chem. Soc., Faraday Trans.* **94**, 1035 (1998)
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- [14] C. H. Gu, H. Li, R. B. Gandhi, K. Raghavan, *Int. J. Pharm.* **283**, 117 (2004)
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07: 3D Mapping of Reciprocal Space with Synchrotron Light

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In a diffraction experiment correlated static or dynamic disorder manifest itself in structured diffuse scattering. Thanks to the availability of bright synchrotron radiation and fast area detectors with high dynamic range, diffuse intensity can readily be observed even for weakly scattering compounds. Moreover, for many cases diffuse intensity can be represented in form of 3D distributions in reciprocal space. These distributions can be now measured with a high level of sensitivity and in a relatively short time. As illustrations, we show examples of reciprocal mapping for the Kohn anomaly in zinc, chemical disorder in a Prussian Blue analogue and a perovskite, thermal diffuse scattering in quartz, in an Invar alloy, and in hexagonal Ice, as well as diffuse scattering in a relaxor ferroelectric.

We will also present a project of new diffractometer, to be installed at beamline BM1A (SNBL at ESRF), that combines a fast pixel detector PILATUS 2M with a flexible 3-axis kappa goniometer. Funding for this instrument has now been received from the Swiss National Science Foundation and the Norwegian Research Council. The diffractometer is designed as a fast mapper of reciprocal space; it will allow us to combine accurate and complete Bragg data with a full sphere 3D map of diffuse scattering measured within a few minutes. Some basic parameters of this diffractometer will be given, and possible modes of data collection will be discussed.

08: High Temperature in-situ XRD Studies on New Solder Materials for MEMS Packaging Applications

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In the fabrication of Micro Electro Mechanical Systems (MEMS), the application of advanced packaging methods involves the development of new solder materials with improved properties [1]. The joining of advanced metallic alloys is limited by high brazing or soldering temperatures. The nanoscale effect of melting point depression (MPD) offers a possibility of lowering the filler metal melting temperature without the compromises resulting from alloying [2].

In-situ high temperature XRD studies have been conducted in order to follow the melting behavior of mixed metal nano-layer systems (Figure 1) and to have a direct observation not only on the materials melting points but also on the formation of intermetallic phases. The influence of internal and external interfaces in the material is crucial and has also been studied.

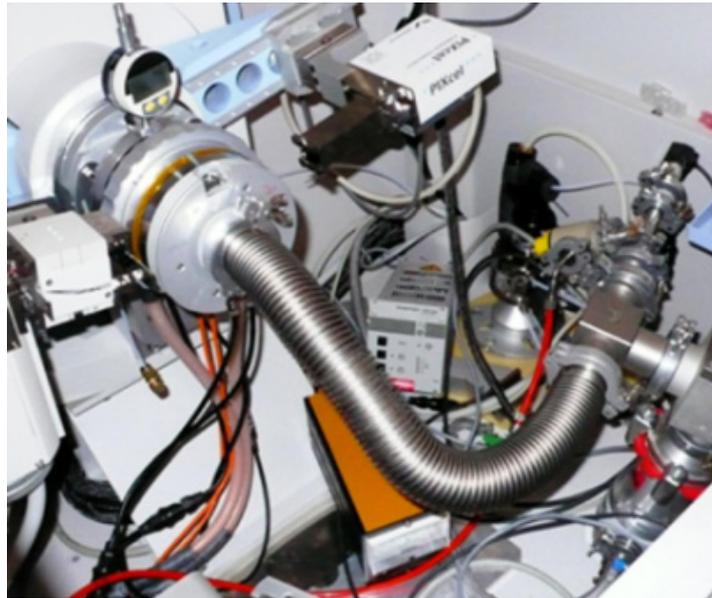


Figure 1.

The MPD effect has been studied for nanolayer brazing fillers in a multilayer system in which the layers of the brazing filler are separated by diffusion barrier layers (DBLs). The example of the AgCu/AlN nano-layer system is shown in Figure 2. The analysis shows that for the 7.7 nm thick AgCu layers, a decrease of 25°C for the melting point was observed for the AgCu/AlN nanolayer configuration. In this case, the eutectic AgCu brazing filler separates in two single phases and the local material interfaces Ag/AlN, Cu/AlN are formed.

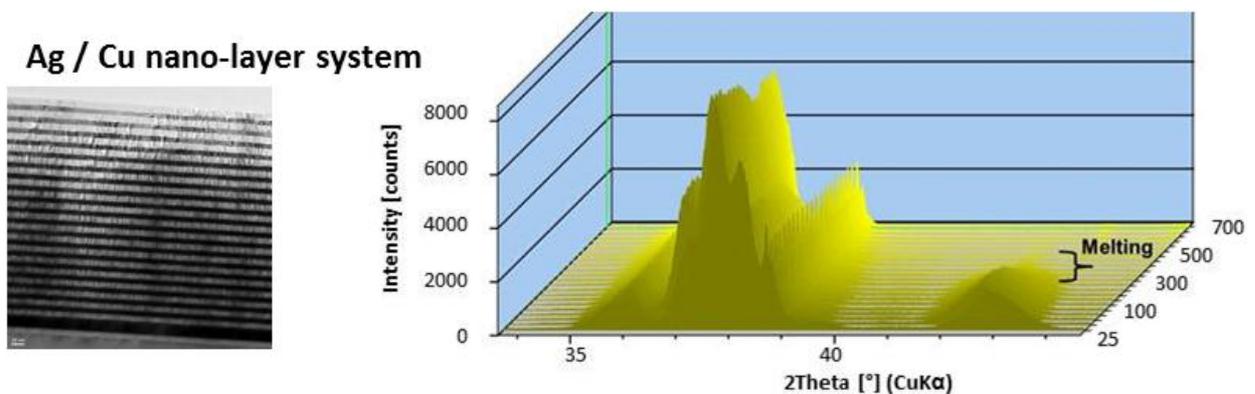


Figure 2.

- [1] "Reliable hermetic MEMS chip-scale packaging" G. Spinola Durante, R. Jose Jamesa, C. Bossharda, C. Muller, J. Baborowski, A. Pezous, F. Cardot, M.-A. Dubois, A. Neels, A. Dommann, EMPC2011, Brighton, UK, 2011.
- [2] "Nanoscale effect-based melting point reduction for brazing filler metals", Empa Activities 09/10, V.Bissig, J.Janczak, p.8.

09: Latest Results from CMOS detector technology

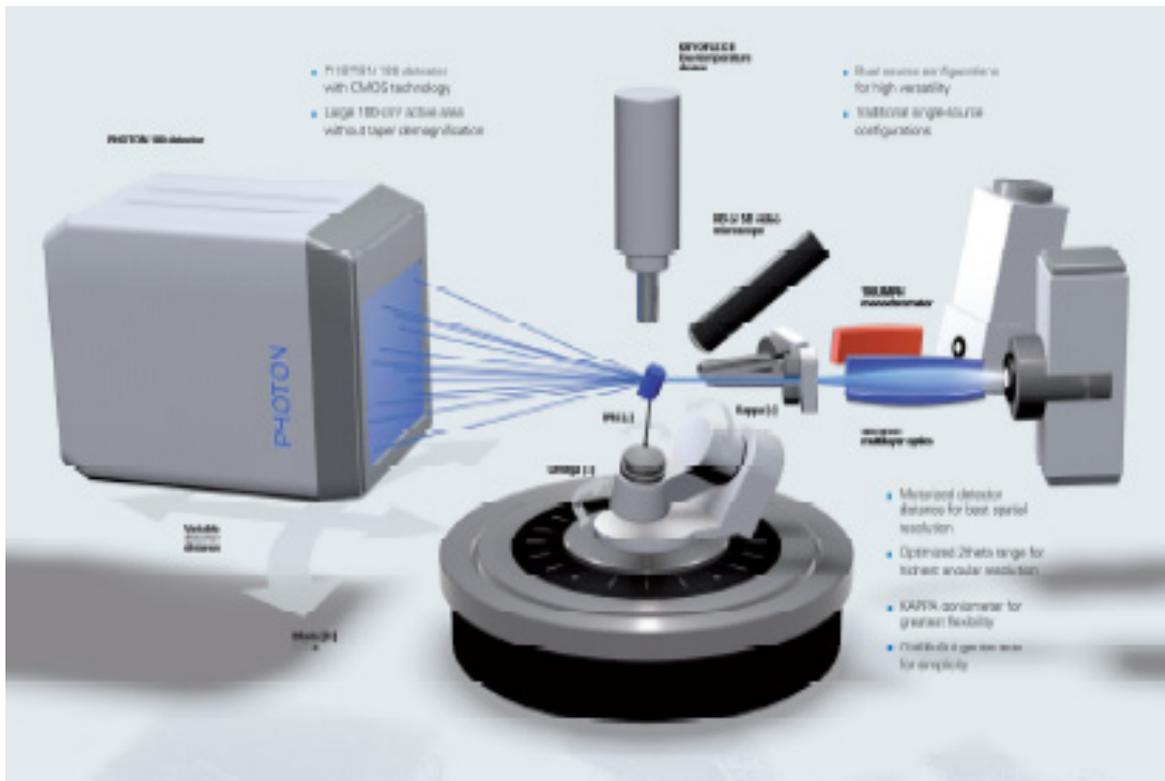
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Detectors for crystallographic applications require a unique combination of sensitivity, speed, dynamic range, resolution and detector size. CMOS (Complementary Metal Oxide Sensor) technology has shown great potential to provide sensors for the next detector platform of choice and has incited a significant wave of advancement in high-performance crystallographic imaging. CMOS technology provides large high-performance sensors that were previously not achievable with CCD manufacturing processes.



Results, as recently obtained in our application laboratory, on a wide variety of samples and applications, from high-pressure to charge density measurements will be discussed

Poster Abstracts

P01: Precursors for oxide materials

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Heterometallic compounds can be used in different applications, for instance as precursors for photo-electronic devices or mixed metal oxides in high- T_c superconductor (e.g. YBCO) [1]. A synthetic strategy to obtain mixed metal oxides is to use decomposition techniques like (metal-organic) chemical vapour deposition (MO-CVD) to combust metal-containing volatile complexes. For the drastic decomposition process, it is suggested to use simple ligand systems which can easily be prepared in large scale. Complexes should then be easily obtained.

In previous work [1], a mixed metal complex of barium and copper was obtained. To obtain a tri-metallic complex with barium, copper and yttrium, the idea of a co-ligand for yttrium came to mind. The beta-diketonates seems to be good co-ligand because yttrium is a hard ion and this kind of ligand are also hard (even more when deprotonated) [figure 1].

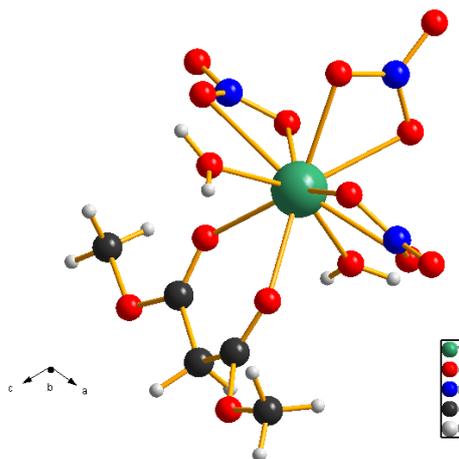


Figure 1: Yttrium complex with dimethylmalonate

- [1] F. Gschwind, O. Sereda, K. M. Fromm, *Inorg. Chem.* **48** (22), 10535-10547 (2009)

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Ion conducting materials are of increasing interest predominantly due to the commercial interest in solid oxide fuel cells and Li batteries. The layered oxide phases of LiM_xO_y ($M = \text{Co}, \text{Ni}, \text{Mn}, \text{Fe}$) are often used as cathode materials for these batteries [1- 3]. While the search for new materials continues to attract considerable attention there has been a noticeable increase in research of new precursors for those materials. Metal alkoxides have been proposed like good precursors due to their high solubility, low decomposition temperatures, cross linking ability, ease of modification and commercial availability [1, 4, 6]. Moreover, recent research [5] showed the use of binary iron/lithium organometallic complexes as single source precursors to solid state cathode materials for potential Li-Ion Battery applications.

For this purpose, we developed new metal alkoxides (e. g. Fig.1) using the halides of iron, nickel, cobalt, and manganese as starting materials. We will present the first results of this work using the Schlenk techniques to synthesize those precursors, which can come as molecular species or as coordination polymer networks (or metal organic frameworks, MOFs).

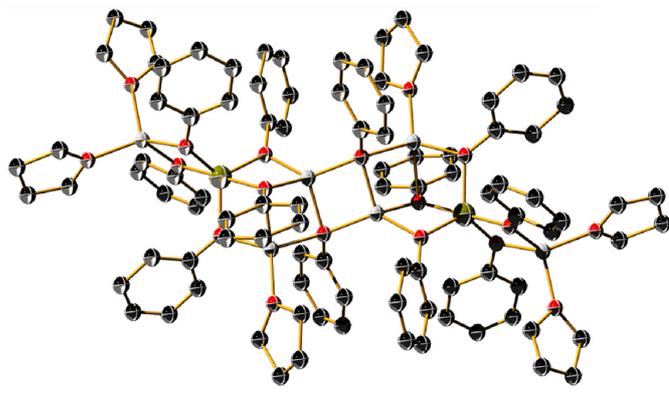


Figure 1: Single Fe-Li-compound with structure formula: $((\text{THF})_6\text{Li}_6\text{Fe}_2(\text{OPh})_{10})_4$

- [1] Jacoby, M.; Chem. Eng. News 76(1998), 37.
- [2] Timothy J. Boyle and al. ; Chem. Mater 15(2003), 3903.
- [3] Yang S.-H and al.; Nature Mat. 2(2003), 464.
- [4] Donald C. B.; Chem. Rev. 89(1989), 1317.
- [5] J. Khanderi, and al.; Inorganica Chimica Acta 370 (2011) 254.
- [6] A. Crochet, JP. Brog, K. M. Fromm, patent filed, June 28th 2010, N° 0143/10

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A variety of structures have been solved using the Powder Charge Flipping algorithm [1, 2] incorporated in program *Superflip* [3, 4]. But, as the program is relatively new, the selection of the values for the input parameters has been rather arbitrary. Therefore, a systematic study answering the questions about the effect of the different input parameters on structure solution; minimum data resolution that can be used and use of the information obtained from the other sources was undertaken.

The data collected for one inorganic (1) and one organic (2) compound were used for these tests.

(1) The original solution (*Superflip*) of zirconium phosphate structure did not have the correct symmetry (P-1), and a few of the atoms in Zr-O-P layers and the quinolinium ions between the layers were missing [5]. Combination of input parameters that deal with: defining the groups of overlapped reflections, repartitioning the overlapped reflections, and the isotropic displacement factor were tested within a sensible range, and an optimal parameter set could be established. With this set, a complete layer structure exhibiting the correct symmetry was produced.

(2) For ribose [6], extensive tests on *Superflip* input parameters did not result in a satisfactory structure solution. Reasoning that starting with non-random phases might help, chemically feasible structures were generated using the direct-space program FOX [7]. None of these were correct. But, using their phases as seeds for generating phase sets in *Superflip* resulted in slightly better solutions. It was only when threshold for flipping was reduced, and establishing the definition of the groups of the overlapped reflections was reoptimized that fully interpretable solutions with the correct symmetry were obtained.

In both cases, the input parameter set was reoptimized for the lower resolution data. For the zirconium phosphate, the structure could be solved even with 2.4 Å resolution data, and the quality of the solutions was insensitive to the input parameters. For ribose, complete solutions were obtained down to the resolution of 1.18 Å when the input parameters were reoptimized.

- [1] G. Ozlányi, A. Sütö, *Acta Crystallogr. A* **60**, 134-141 (2004)
- [2] G. Ozlányi, A. Sütö, *Acta Crystallogr. A* **61**, 147-152 (2005)
- [3] L. Palatinus, G. Chapuis, *J. Appl. Crystallogr.* **40**, 786-790 (2007)
- [4] Ch. Baerlocher, L.B. McCusker, L. Palatinus, *Z. Kristallogr.* **222**, 47-53 (2007)
- [5] L. Lju et al *Inorg. Chem.* **48**, 8947-8954 (2009)
- [6] D. Šišak et al *Angew. Chem. Int. Ed.* **49**, 4503-4505 (2010)
- [7] V. Favre-Nicolin, R. Cerny *Z. Kristallogr.* **219**, 847-856 (2004)

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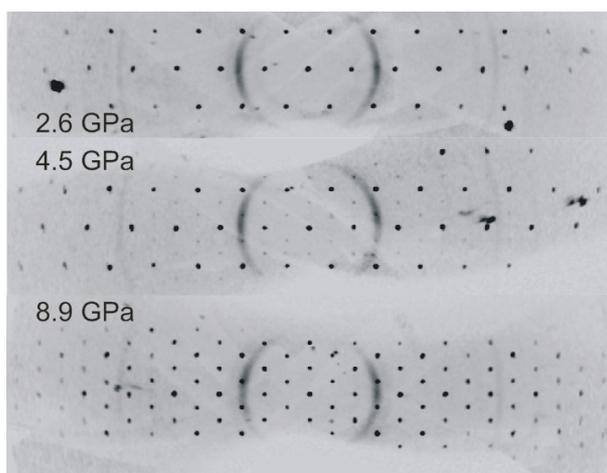
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The mineral benitoite, $\text{BaTiSi}_3\text{O}_9$, is remarkable in many respects: Not only is it a well-priced gemstone with strong pleochroism, but it is also used in electron microprobe laboratories as standard material and for alignment of the electron beam due to its fluorescence. The basis of the structure is a mixed framework of $\{\text{Ti}[\text{Si}_3\text{O}_9]\}^{2-}$, composed of discrete Ti octahedra and $[\text{Si}_3\text{O}_9]$ triple rings. Ba atoms lie in columns between the triple rings giving the overall symmetry of the very rare space group $P-6c2$ _{1,2}.

In-situ high-pressure single-crystal diffraction of $\text{BaTiSi}_3\text{O}_9$ shows additional Bragg peaks above 3.70 GPa indicating a non-isomorphous transition from $P-6c2$ (no.188) to $P31c$ (no.159) space group symmetry with $a' = a\sqrt{3}$.

Fig 1: Reconstructed $hk4$ reciprocal layer in Benitoite, $\text{BaTiSi}_3\text{O}_9$ with increasing pressure.



The crystal structure investigations reveal the off-centre displacement of the Ba atoms on release of symmetry constraint to be responsible for the high compressibility of the high-pressure form. The triple ring in the Benitoite structure loses the mirror symmetry resulting in an increasing deviation from 90° of the angle spanning between the connecting line between the terminal oxygen atoms of the silicon tetrahedra and the central ring plane from 0° at the phase transition to a maximum of 15° at 8,88 GPa. Similar behaviour with pressure has also been observed in closely related $\text{K}_2\text{ZrSi}_3\text{O}_9$, wadeite, as well as other cyclosilicates with triple rings of silicate tetrahedra³.

[1] W. Zachariasen, Z. Kristallogr. **74**, 139 (1930).

[2] K. Fischer, Z. Kristallogr. **129**, 222 (1969)

[3] V. Kahlenberg, J. Konzett & R. Kaindl, J. Solid State Chem **180**, 1934 (2007)

P05: Crystal structure of the uranyl mineral grimselite,
(K_{2.43}Na_{0.57})_{Σ3.00}Na[(UO₂)(CO₃)₃](H₂O), from Jáchymov, Czech Republic

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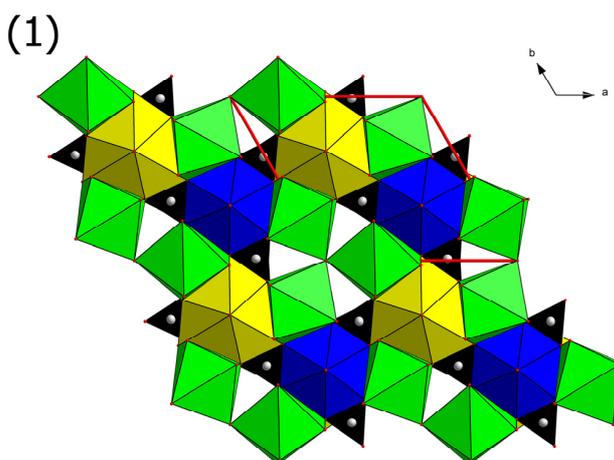
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The crystal chemistry of uranium compounds is of high importance due to environmental impacts connected with the long-term underground depositories of „spent nuclear fuel” (SNF) [1]. Despite of considerable improvement of our knowledge of crystal chemistry of U⁶⁺, studies carried out on natural minerals are important. Here we present the refinement of the crystal structure of the uranyl mineral

grimselite, determined for the first time by single-crystal X-ray diffraction on a natural specimen, found at Jáchymov, Western Bohemia, Czech Republic. The crystal structure of the synthetic analogue is known [2]. Grimselite was firstly reported from a cable tunnel between Gersteneegg and Sommerloch in the Grimsel area, Aarmassif, Switzerland [3].

The starting model of the synthetic analogue [2] refined with JANA2006 [4] to $R_1 = 0.0082$, $wR_1 = 0.0185$ with GOF = 1.33. Natural grimselite is hexagonal, of the space group $P-62c$, $a = 6.7050(3)$, $c = 13.2857(5)$ Å, $V = 595.74(3)$ Å³; the structural formula derived from the refinement is (K_{2.43}Na_{0.57})_{Σ3.00}Na[(UO₂)(CO₃)₃](H₂O), $Z = 2$. Crystal structure of natural grimselite is built upon heteropolyhedral sheets **(1)**, consisting of uranyl hexagonal bipyramids (blue), linked by trigonal planar CO₃²⁻ groups (black) to NaO₈ (yellow) and (K, Na)O₈ (green) polyhedra. In contrast to the synthetic analogue, natural grimselite has a mixed Na, K occupation of KO₈ polyhedra. Results of the structure refinement are supported by chemical analysis (EPMA–WDS) and vibration spectroscopy (IR and Raman).



[1] P.C. Burns, A.L. Klingensmith, *Elements*, **2**, 351 (2006)

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[4] JANA2006: The crystallographic computing system. Institute of Physics, Praha, Czech Republic by V. Petříček, M. Dušek, L. Palatinus (2006)

P06: Crystal structures and microstructures of ordered and disordered kalsilites.
Is kaliophilite a KAlSiO_4 polymorph or kalsilite polytype?

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Despite of numerous investigations using various experimental techniques, the problem of polymorphism in feldspathoid KAlSiO_4 is still not solved. Recent discovery of a new polymorph called magakalsilite [1] or investigations of possible phase transitions in kalsilite [2] are significant steps in the right direction. However, existing results about the KAlSiO_4 system are extremely complex and often controversial.

Literature suggests that a completely satisfying structure model of kalsilite does not exist and that the crystal structure of kaliophilite is still unknown.

As a part of on-going research in this system, we have investigated two X-ray powder diffraction patterns that correspond to ordered and disordered states of kalsilite (KAlSiO_4). Rietveld refinement of both experimental patterns in two different space groups $P6_3$ and $P3$, inspection of electron density maps and microstructural characteristics revealed disordered layers of type A and B (Fig1) i.e. stacking faults characteristics of disordered kalsilite. Based on the unit cell values and analysis of the layer disorder, we postulate that the here described disordered kalsilite structure corresponds to synthetic kaliophilite. Therefore, kaliophilite is not a KAlSiO_4 polymorph but a kalsilite polytype characterized by random disorder for A and B layers stacked along the c -axis.

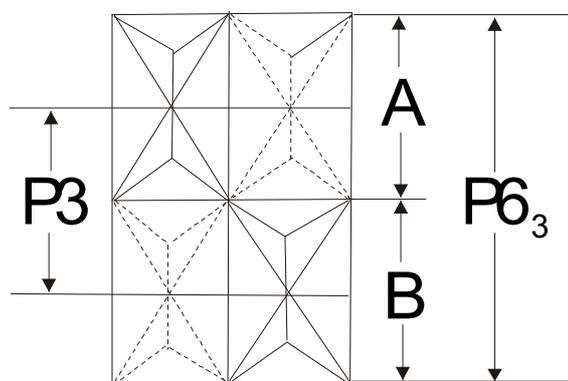


Fig.1 Schematic representation of two types of layers in disordered kalsilite in $P6_3$ and $P3$ groups

[1] A.P. Khomyakov, G.N. Nechelyustov, E. Sokolova, E. Bonaccorsi, S. Merlino, M. Pasero, *The Canadian Mineralogist*, **40**, 961 (2002)

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P07: Vibrational (FT-IR and Raman) spectral studies, geometrical parameters and theoretical calculations of triethylenetetramine and its cyano-bridged heteronuclear polymeric complex

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In our previous studies [1, 2], the experimental results of the vibrational spectroscopic, thermal and structural analysis of the cyano-bridged heteronuclear polymeric complexes, $[\text{Cd}(\text{teta})\text{Ni}(\mu\text{-CN})_2(\text{CN})_2]\cdot 2\text{H}_2\text{O}$ and $[\text{Zn}(\text{teta})\text{Ni}(\mu\text{-CN})_2(\text{CN})_2]_n$ were investigated. In this study we report on the molecular geometry and vibrational frequencies of triethylenetetramine (teta) and its cyano-bridged heteronuclear polymeric complex, $[\text{Zn}(\text{teta})\text{Ni}(\mu\text{-CN})_2(\text{CN})_2]_n$. The molecular geometry and vibrational frequencies of triethylenetetramine (teta) in the ground state has been calculated using the density functional method (B3LYP) with 6-311++G(d,p) basis set. The optimized geometric bond lengths and bond angles were obtained by DFT (B3LYP) had provided the best agreement with experimental data. Furthermore, we attempt a theoretical investigation of the metal-ligand vibrational modes, which will be discussed in detail in the second part of the study. The molecular geometry was optimized from Density Functional Theory (B3LYP method) using LANL2DZ basis set on the ground state and the infrared wavenumbers and intensities were predicted by using this geometry. Calculated wavenumbers and intensities were compared with FT-IR and Raman spectra of triethylenetetramine and its cyano-bridged heteronuclear polymeric complex. Additionally, time depended density functional theory (TD-DFT) method using 6-311++G(d,p) basis set was used to determine the minimum energy structure of the complex. According to the calculated results, the vibrational wavenumbers, geometric parameters and excitation energies show an excellent agreement with the experimental data.

[1] G.S. Kurkcuoglu, T. Hokelek, O.Z. Yesilel, S. Aksay, Struct. Chem. 19 (2008) 879.

[2] G.S. Kurkcuoglu, O.Z. Yesilel, I. Kavlak, O. Buyukgungor,
Zeitschr. für anorg. Allgem. Chem., 635 (2009) 175.

P08: Hetero-Metallic Coordination Polymers: Crystal Structures of trans-[M(*N-Meim*)₂Ni(μ-CN)₄]_n (M=Cu(II), Zn(II) and Cd(II))

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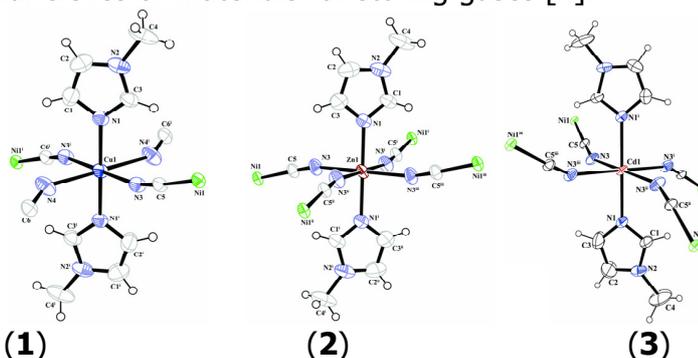
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Cyano complexes were among the first coordination compounds ever prepared, studied, described and used [1, 2] and they are still under investigation in coordination and organometallic chemistry at present [3]. These compounds are interesting as ion exchangers, molecular sieves or materials for storing gases [4].



In this study, three cyano bridged heterometallic complexes of general formula, trans-[M(*N-Meim*)₂Ni(μ-CN)₄]_n (*N-Meim* = N-methylimidazole and M = Cu(II), Zn(II) and Cd(II)) have been synthesized. The crystallographic analyses reveal that the complexes, [Cu(*N-Meim*)₂Ni(μ-CN)₄]_n (**1**), [Zn(*N-Meim*)₂Ni(μ-CN)₄]_n (**2**) and [Cd(*N-Meim*)₂Ni(μ-CN)₄]_n (**3**), have polymeric 2D networks. In the complexes, four cyanide groups of [Ni(CN)₄]²⁻ coordinated to the adjacent M(II) ions and distorted octahedral geometries of complexes are completed by two nitrogen atoms of trans *N-Meim* ligands. Although the literature lists many reports on the binding modes of tetracyanonickelate(II) complexes, from the X-ray crystal structure point of view only a limited number of structures with corrugated and four cyanide-bridged polymeric networks have been obtained until now. The Cu(II) and Zn(II) complexes are the first examples showing coordinated 2D layered structures with four cyanides.

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P09: Structure Analysis of Two Open-framework Zirconium Phosphate Materials

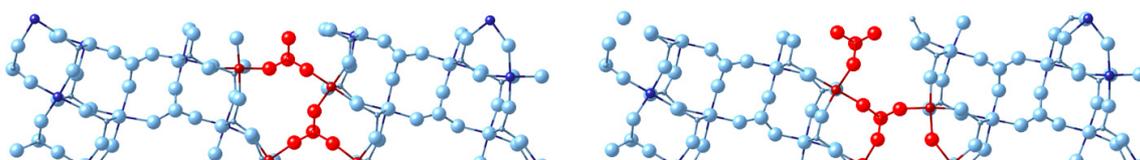
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The structures of the ZrPOF materials synthesized in the presence of ethylamine (EA) and diethylamine (DEA) have been analyzed. As the synthesis conditions and diffraction patterns were similar, few structural differences were expected. However, while the ZrPOF-EA structure is solved and refined [1], the ZrPOF-DEA structure displays some ambiguities.

The powder pattern of ZrPOF-DEA could be indexed with an orthorhombic unit cell comparable to that of ZrPOF-EA. An initial structural model was derived using the powder charge flipping algorithm [2], implemented in the program *Superflip* [3]. Rietveld refinement revealed that ZrPOF-DEA has adopted the symmetry $Pmc2_1$ ($a = 6.623$, $b = 37.171$ and $c = 20.033$ Å) whereas ZrPOF-EA crystallizes in the higher space group $Pbam$ ($a = 19.957$, $b = 37.067$ and $c = 6.617$ Å). Thus, ZrPOF-DEA contains a total of 124 framework atoms (16 Zr, 24 P, 84 O/F) in the asymmetric unit, which is double that of ZrPOF-EA. Even though the two structures display common features, the refinement of ZrPOF-DEA has not yet been successfully completed. Only one of the diethylamine ions has been located and there appears to be some additional disorder in the framework that still needs to be addressed.



The model obtained for ZrPOF-DEA from charge flipping (left) deviates slightly from the ZrPOF-EA model (right). The differences in connectivity are indicated in red.

- [1] L. Liu *et al.*, *Angew. Chem. Int. Ed.* DOI:10.1002/anie.201102738
- [2] Ch. Bärlocher *et al.*, *Z. Kristallogr.* **222**, 47 – 53 (2007)
- [3] L. Palatinus and G. J. Chapuis, *Appl. Crystallogr.* **40**, 786 (2007)

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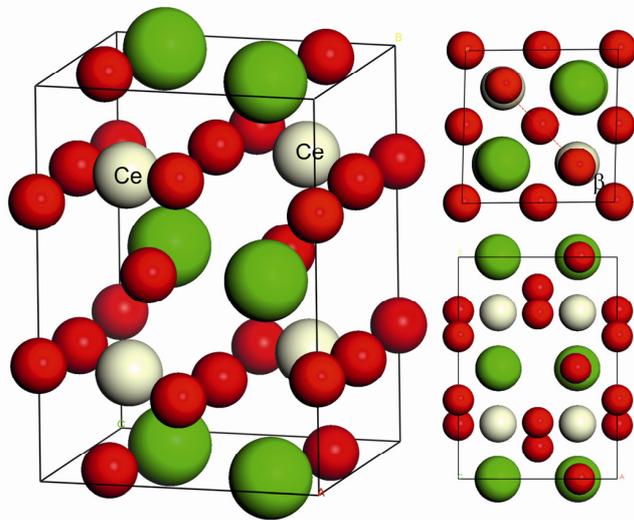
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The proton conducting perovskites are extensively studied for their potential use in fuel cells, electrolyzers and gas sensors. Recent Empa data show that the proton transport activation energy scales linear with the lattice constant, suggesting that an enlarged lattice volume – for example thin films with epitaxial strain - can promote proton conductivity. To comprehend the interaction of water with the oxide lattice, and the underlying transport mechanisms, we combine electrochemical transport measurements *in-situ* with synchrotron and neutron spectroscopy and scattering methods. Optical Raman spectroscopy and XRD studies on the compressively strained BaCe_{0.8}Y_{0.2}O_{3-δ} proton conductors indicated that the proton transport may be anisotropic. The effect of hydration was studied by *in-situ* XPS, where the reactions of water on its surface were revealed.



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P11: Perfect Epitaxial Growth of Germanium on Silicon and Crystal Quality Quantification by High-resolution X-ray Diffraction

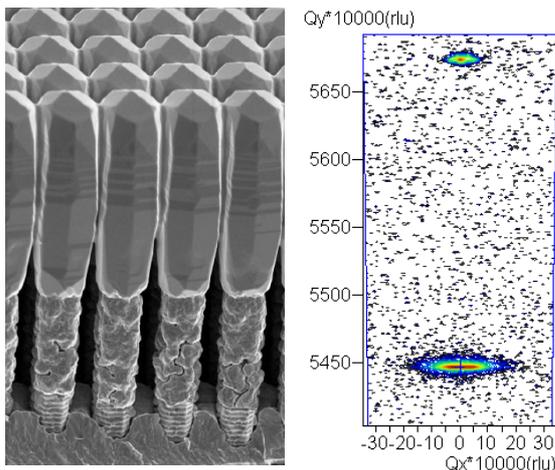
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The epitaxial growth of germanium on silicon allows for the integration of germanium into silicon CMOS technology, availing in standard ICT devices the superior properties of germanium as high electron density and high electron mobility. Nevertheless, layer stresses have been observed being responsible for wafer bowing and in some cases layer cracking. The observed layer stress is a result of the lattice mismatch between the germanium and the silicon and the high mismatch of thermal expansion coefficients of germanium and silicon [1].



A new approach for the germanium deposition on silicon has been introduced with the use of a patterned silicon substrate. This innovative approach results in a complete relaxation of the germanium being epitaxially grown on the Si pillar substrate. The threading dislocation density is also reduced to close to zero and a perfect crystal quality is obtained despite the large lattice mismatch. No layer cracking and a minimized wafer bowing is observed which presents an innovative key technology to wafer handling and post-growth processing.

Fig. 1. Left: SEM view of 8 μm Ge towers on Si pillars. The high crystal quality is apparent by the growth along the crystal planes and is confirmed and quantified by HRXRD angular scans and RSMs. Right: RSM of the (004) reflections of Si (top) and Ge (bottom). The FWHM of the Germanium (004) $\omega/2\theta$ -reflection is 16 arcsec.

The crystalline quality was investigated by High Resolution X-Ray Diffraction (HRXRD) using symmetrical (004) and asymmetrical (224) reflections and measuring angular scans and Reciprocal Space Maps (RSMs). These measurements allowed for a quantification of the crystal mismatch, the layer tilt and the degree of relaxation. It was shown that layers up to 50 μm thicknesses could be grown showing 100% relaxed and perfectly parallel germanium layers with respect to the silicon substrate crystal.

This is a large step towards the integration of germanium into the silicon technology which is particularly interesting for future solid-state X-ray detectors where germanium is highly superior to silicon having an X-ray absorption coefficient being ~ 25 higher than silicon.

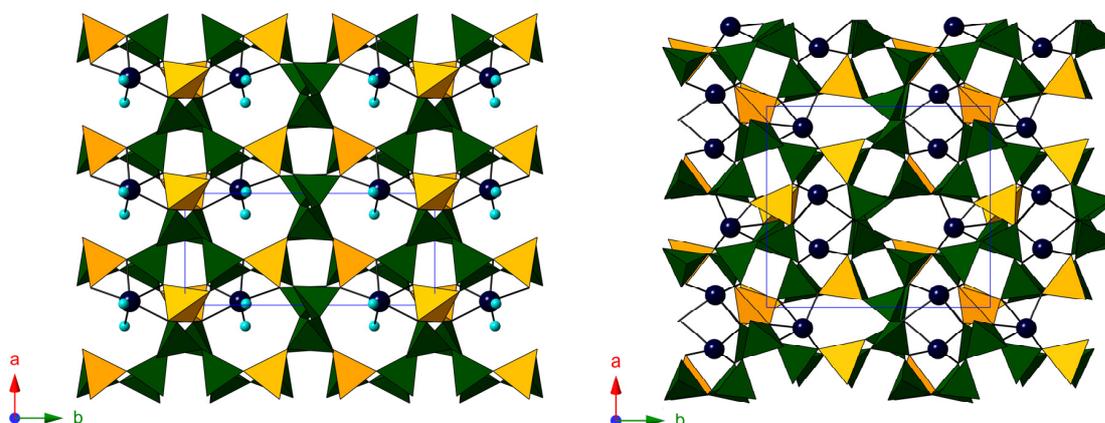
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P12: Stepwise in situ dehydration of yugawaralite: a temperature dependent single-crystal X-ray study

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Yugawaralite $\text{CaAl}_2\text{Si}_6\text{O}_{16} \cdot 4\text{H}_2\text{O}$, space group $\mathcal{P}c$, is a natural zeolite. The tetrahedral framework ([1] -[4]) consists of well ordered Si (green) and Al (yellow) tetrahedra (Figs.). At room temperature 8-coordinated Ca is located at the intersection of the channels and is bound to four framework O and four H_2O molecules. Single-crystal dehydration was performed under a dry nitrogen atmosphere in steps of 25°C up to 325°C . According to structure refinement yugawaralite loses $1\text{H}_2\text{O}$ pfu below 50°C triggering a small change in the unit cell parameters. At 300°C Ca is reduced to six-fold coordination, bonding to W1 and W2 and four framework O with little change in the cell parameters (left Fig.). Above 300°C dehydration proceeds resulting in a decrease of coordination of Ca, which now bonds to five framework O [5, 6]. The structure transforms to space group $\mathcal{P}n$ resulting in a doubling of the a -axis (right Fig.) leading to complicated intergrowth and twinning. The partially occupied Ca sites compress the channels yielding a 7.11% reduction of (normalized) volume.



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P13: Spin Density Distribution of the orbital singlet Mn(II):
“A polarised and non-polarised neutron diffraction study of the
[Mn(Imz)₆]²⁺(NO₃)₂ complex, where Imz = Imidazole”

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The degree of covalency of the Mn – N bond in manganese(II)-histidine interactions, has been of interest due to the vital role manganese(II) play in biological systems.¹ In this work, polarised neutron diffraction (PND) and unpolarised neutron diffraction, multipolar least square analysis (MPLSQ),^{2,3} Density Functional Theory (DFT)⁴ calculations and assessment, will be used to understand the Mn²⁺ spin density distribution in the complex [Mn(Imz)₆]²⁺(NO₃)₂. Firstly, within the trigonal unit cell for the complex, while correlating these results to the local anisotropic axis of the unit cell. And, lastly, using these results in understanding the spin density distribution, and π -anisotropy, effect about the Mn – N bond.

For the Mn(II) ion, where the orbital angular momentum $L = 0$, and which is represented by the 6A_{1g} ground state, the spin density distribution of the unpaired d-electrons is defined by a superposition of one-center density population orbital product functions. Multipolar expansion provides a representation of these orbital functions in the spin density form factor description.

Through multipolar expansion computation,³ the spin density structure factors, derived from the flipping ratios of polarised neutron diffraction, can be correlated to the population of respective multipoles, and thus orbitals. We have performed a PND experiment on the D3, and a non-polarised neutron diffraction experiment on the D9, instruments at the ILL in France, on a 2×2.5 × 5 mm³ (40 mg) crystal of the deuterated [Mn(Imz)₆]²⁺(NO₃)₂ complex. We have also performed DFT calculations and modelling on this system.

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The term "intercluster compound" refers to assemblies that are constituted of at least two different large, inorganic building blocks [1, 2]. A few intercluster compounds already exist and it has been possible to determine their crystal structures by single crystal X-ray diffraction.

These results deliver insights into the arrangement of large building units in the solid-state material and the underlying intermolecular forces [3, 4].

These first results show that intercluster compounds are very promising for the study of structural and physical properties of nanosized particles.

They also open a wide range for new applications (lithography techniques, electronic or optical devices, study of quantum effects and also of orbital bands). Since only a few compounds have been studied, there is a huge potential for new discovery in this field. We would like to present new building blocks [5] and their corresponding intercluster compounds.

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The bond between transition metals has always attracted structural chemists, because of the intriguing features that characterize this interaction. In particular, Mn-Mn bond in $\text{Mn}_2(\text{CO})_{10}$ is one of the most characterized, because of the historical importance of this molecule [1]. Spectroscopic characterizations at high pressure have also been reported, suggesting the occurrence of a phase transition above 0.8 GPa producing a conformational change (from staggered to eclipsed) [2]. This transformation would be very similar to that we observed on species like $\text{Co}_2(\text{CO})_6\text{L}_2$ ($\text{L}=\text{AsPh}_3, \text{PPh}_3$) [3].

However, periodic DFT calculations and X-ray powder diffraction are not in agreement with the reported interpretation of the Raman spectra. Indeed, no conformational change is observed on increasing the pressure, but a curious rotation of the two $\text{Mn}(\text{CO})_5$ moieties, leading to an unprecedented Mn-Mn off-axis bond (the Mn-Mn bond does not coincide with the Mn-CO apical axis, as in the gas phase molecular structure, see the Figure). Interestingly, this molecular geometry can be anticipated also from diffraction at ambient pressure, because the molecule shows an incipient distortion. Single crystal data at high pressure are not possible, because the samples easily break upon application of the pressure.

Theoretical calculations within the interacting quantum atom approach are also used to discuss the new geometry.

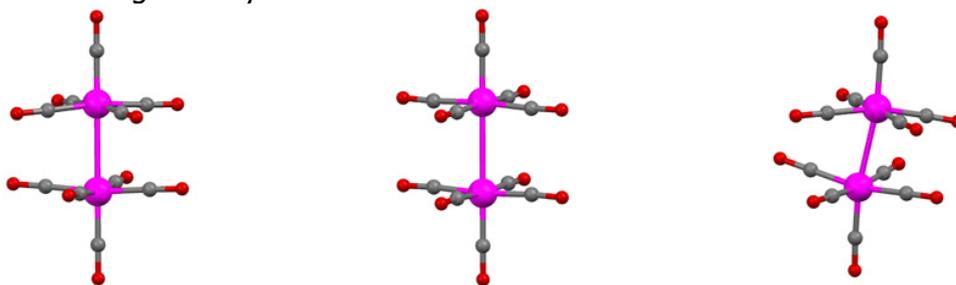


Figure 1. Left: the molecular conformation of $\text{Mn}_2(\text{CO})_{10}$ at ambient condition (staggered). Centre: the molecular conformation at 3GPa as hypothesized from Raman spectroscopy (eclipsed). Right: the conformation of $\text{Mn}_2(\text{CO})_{10}$ at 3GPa from P-DFT theoretical predictions and XRPD experiments.

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P16: On the purity of multi-layer focused X-ray radiation

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Multilayer optics are currently adopted in many laboratories for single crystal diffraction, using very low power X-ray generated by micro-sources. The high-brilliance and the micro-focusing are the main advantages of these radiation sources, that allow high performance experiments also on a laboratory scale.

However, we recently discovered [1] a fundamental defect of this technology, namely the significant contamination of the characteristic radiation by low energy photons which are reflected by the mirrors because of the small incidence angle. Simple experiments show that the contamination can significantly reduce the accuracy of measured intensities, especially when Mo K α radiation is used.

We have therefore proposed a simple and economic solution to the problem [1]: an aluminium filter of adequate thickness efficiently removes the low energy contaminant photons. Performances of Al-filtered data collections are reported and alternative solutions are discussed.

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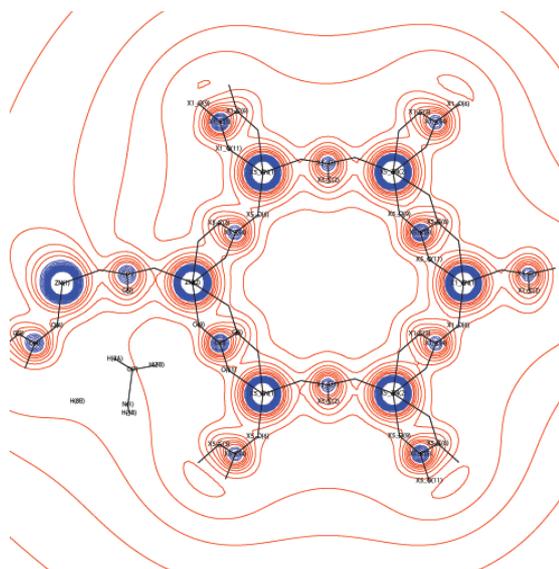
P17: Properties of metal oxalate materials from electron density. Modelling the building blocks and evaluation of framework interaction

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Extensive research work has been carried out in last few decades on the synthesis and characterisation of several metal organic materials including carboxalates, phosphates, and arsenates [1]. To a large extent, the interest is due to the interesting properties possessed by the materials and potential applications, such as electrical conductivity, magnetism, photo mechanism, host-guest chemistry etc. We focused our attention to metal oxalates, testing the possibility to model electron density of building blocks and obtain at least approximate evaluation of the properties. In these materials, the oxalate ion often acts as a rigid bidentate ligand



which bridge metal centres [2] therefore facilitate the formation of extended structures with dimensionalities ranging from zero to three [3].

New inorganic–organic hybrid structures based on Zinc oxalate structures, which show 1D linear, 2D honeycomb and 3D structures were studied. In order to model the building blocks of these frameworks, we used as benchmark some simple structures like $\text{Zn}(\text{C}_2\text{O}_4)$, $\text{Zn}(\text{C}_2\text{O}_4)(\text{H}_2\text{O})$, $\text{Zn}(\text{C}_2\text{O}_4)(\text{C}_4\text{N}_2\text{H}_{10})$, $(\text{HC}_2\text{O}_4)_2(\text{C}_4\text{N}_2\text{H}_{12})$. All compounds were obtained through hydrothermal synthesis. Electron density distribution was studied through X-Ray diffraction and through density functional theory. Once the modelling was refined and tested, the electron densities of 1D-2D-3D framework were computed using multipoles restricted to optimized theoretical building blocks. This allows to reconstruct the electron density of more complex structures, often not available in the form of good quality single crystals. The results are utilised for evaluation of material properties such as electrostatic potential (a Zn oxalate honeycomb is plotted in the Figure), the interaction energies between the framework and neutral guest molecules or counter-ions, and the calculation of the active surface areas of the framework [4].

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P18: Pavlovskyite $\text{Ca}_8(\text{SiO}_4)_2(\text{Si}_3\text{O}_{10})$ - a new mineral of altered silicate-carbonate xenoliths from the two Russian type localities: Birkhin massif, Baikal Lake area and Upper Chegem caldera, Northern Caucasus

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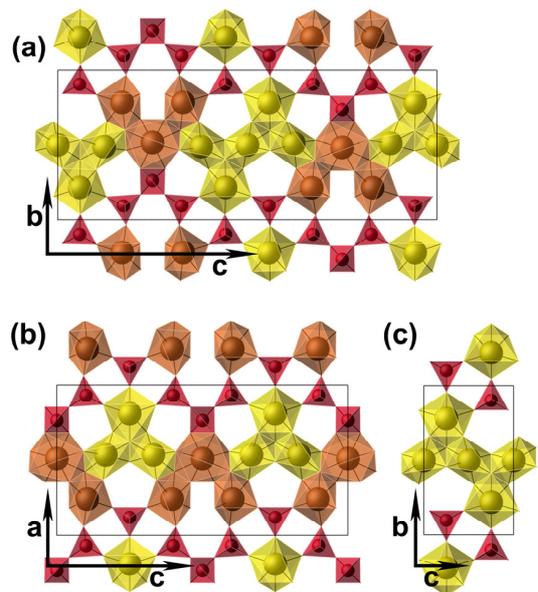
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The new mineral pavlovskyite $\text{Ca}_8(\text{SiO}_4)_2(\text{Si}_3\text{O}_{10})$ occurs at the rims of galuskinite $\text{Ca}_7(\text{SiO}_4)_3\text{CO}_3$ veins cutting calcio-olivine skarns in the Birkhin gabbro-massif (Eastern Siberia). The second type-locality are xenoliths in ignimbrites of the Upper Chegem caldera (Northern Caucasus).

The structure of pavlovskyite **(a)** is a 1:1 member of a polysomatic series with kilchoanite $\text{Ca}_6(\text{SiO}_4)(\text{Si}_3\text{O}_{10})$ **(b)** and calcio-olivine $\gamma\text{-Ca}_2\text{SiO}_4$ **(c)** as end members. The structure consist of calcio-olivine slices interstratified with trisilicate modules of $\text{Ca}_4(\text{Si}_3\text{O}_{10})$ composition. The synthetic analog of pavlovskyite is known from cement like materials [1], but no structure refinement has been done so far.

The crystal structure of pavlovskyite, space group $Pbcn$, $a = 5.0849(1)$, $b = 11.4116(2)$, $c = 28.6304(8)$ Å, $V = 1661.33(7)$ Å³, $Z = 4$ has been refined from X-ray single crystal data to $R1 = 3.99\%$. For comparison with pavlovskyite, the crystal structure of kilchoanite from the Birkhin massif, space group $\bar{I}2cm$, $a = 11.4525(2)$, $b = 5.0867(1)$, $c = 21.996(3)$ Å, $V = 1281.40(4)$ Å³, $Z = 4$ has been refined from single-crystal X-ray [1] Bennet, J.M., Gard, J.A., Speakman, K. and Taylor, H.F.W. (1966) $\text{Ca}_8\text{Si}_5\text{O}_{18}$ and the nature of " γ -dicalcium silicate hydrate". *Nature*, **12**, 1127. data to $R1 = 2.00\%$.



P19: Lithium self-diffusion in $\text{LiAlSi}_2\text{O}_6$ glass and single crystals

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Understanding the mechanisms of lithium diffusion is of great interest for geo- and material sciences. Optimizing the performance of Li-bearing solid media has a significant impact in developing new technologies. Knowledge of kinetic Li-isotopic fractionation leads to better understanding of geological processes in which lithium geochemistry plays a major role.

Our ongoing research is aimed to investigate Li diffusion in aluminosilicate media. In the scope of this study, spodumene ($\text{LiAlSi}_2\text{O}_6$) -like materials were selected as representative model system since lithium, as the only mobile species, migrates through a static aluminosilicate network. Crystalline and glassy materials are compared in order to determine the effect of structural order on Li-diffusion. Glasses were produced by melting of oxide and carbonate mixtures as well as by melting natural spodumene. Natural crystals are from different pegmatites worldwide. Synthetic single crystals were obtained in a slow crystallization process using a flux method. The samples were tested by impedance spectroscopy for ionic conductivity in the range between 1 Hz to 10 MHz at temperatures up to 940 K. Additionally, lithium self-diffusion coefficients were determined by diffusion couple experiments using two halves with same base composition but different Li isotopic abundancies. Li isotope profiles were measured using UV fs laser ablation coupled with ICP-MS. Raman spectroscopy aided in better understanding the local structural features which coordinate lithium migration.

Ionic conductivity was found to be 6 - 7 orders of magnitude slower in natural spodumene crystals than in the glasses while the activation energy for Li conduction is about the same for both materials (0.66 kJ/mol for the glass, 0.76 kJ/mol for the crystal). This implies that the barrier for Li-migration is not sensitive to structural order in aluminosilicate materials. Comparison of Li isotope diffusion data and dc ionic conductivity yields a correlation factor of 0.5 for Li-diffusion in $\text{LiAlSi}_2\text{O}_6$ -glasses.

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Pigment Red 170 is an economically important automotive coating in the paint industry, but subject to fading. Structurally it has four polymorphic forms namely the α , β , γ and δ -polymorph. Among them the γ -polymorph shows superior pigment properties [1]. It has been found that modifications of some of the molecule's substituents can affect the durability, but a rational approach to such modifications requires an understanding of the crystal structure of the pigment. Despite the importance of Pigment Red 170 in many industrial applications only a few structural studies have been carried out [1,2]. Only recently, Schmidt *et al.*, have determined the structures of the α - and γ -phases from a combination of X-ray powder diffraction and crystal structure prediction algorithms [1-2]. According to the description given, both phases have layer-like structures.

Single crystal data of the β -phase have been collected by Schmidt on a sealed tube diffractometer. They show diffuse scattering. We have collected Synchrotron data from the same crystal and found that the observed rods of diffuse scattering are typical of faulted layer stacking. There is currently some uncertainty concerning the correct unit cell that should be used to describe the average structure. The Synchrotron data suggest a larger unit cell than that derived by Schmidt. We will describe our results from the attempts to derive the correct unit cell and solve and refine the average structure.

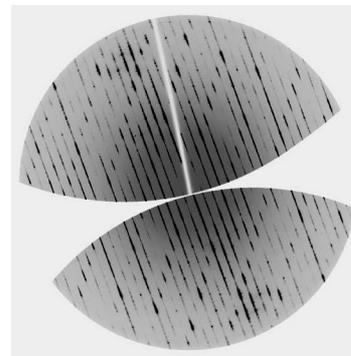


Fig. 1. The $h2l$ reciprocal lattice plane from the β -phase of Pigment Red 170 collected on the BM01A beamline at SNBL (ESRF).

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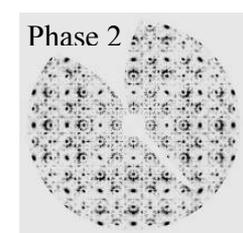
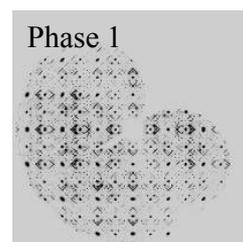
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Hexagonal β - NaLnF_4 (Ln=Y,La-Lu) compounds are a family of up-conversion materials which emit visible light upon IR excitation. Understanding of the properties of these technologically important materials requires a knowledge of their structures at an atomic level [1]. We are presently studying two phases of so-called " α - NaLuF_4 " obtained from the melt with a likely composition of $\text{Na}_5\text{Lu}_9\text{F}_{32}$.

Phase 1 show strong Bragg scattering, commensurate satellite reflections, significant diffuse scattering, while phase 2 shows just strong Bragg reflections with diffuse scattering. The strong, apparently cubic, reflections in reciprocal lattice rows are not collinear and they are split at high angles. This suggests that the crystal is a multiple twin of a structure of lower symmetry with near overlap of reflections. If the satellites are treated as Bragg peaks, an orthorhombic supercell and six fold twinning follow with likely a space group of $Cmmm$. Considering only the positions of heavy atoms in the asymmetric unit of the small cell (based on the apparently cubic reflections), the average structure may be described equally well in two different ways for both the phases. The presence of residual electron density in the difference Fourier map of both descriptions was interpreted in terms of disordered fluorine atoms. Their positions are chemically more meaningful for one of the two heavy-atom models.

For the phase 1 structure, the phases of the superstructure reflections were determined by band flipping [2] implemented in the program Superflip [3]. The reconstructed difference electron density map shows two distinct commensurately modulated parallel columns of cations: one with varying $\text{Na}^+/\text{Lu}^{3+}$ occupancy and one with positional displacements of the ions from the average structure positions. Interestingly, two different solutions result from the band flipping with equal probability. These two solutions differ only by the details of positional and occupational modulation. The two solutions are distinct and the correct one can be identified by subsequent structure refinements.



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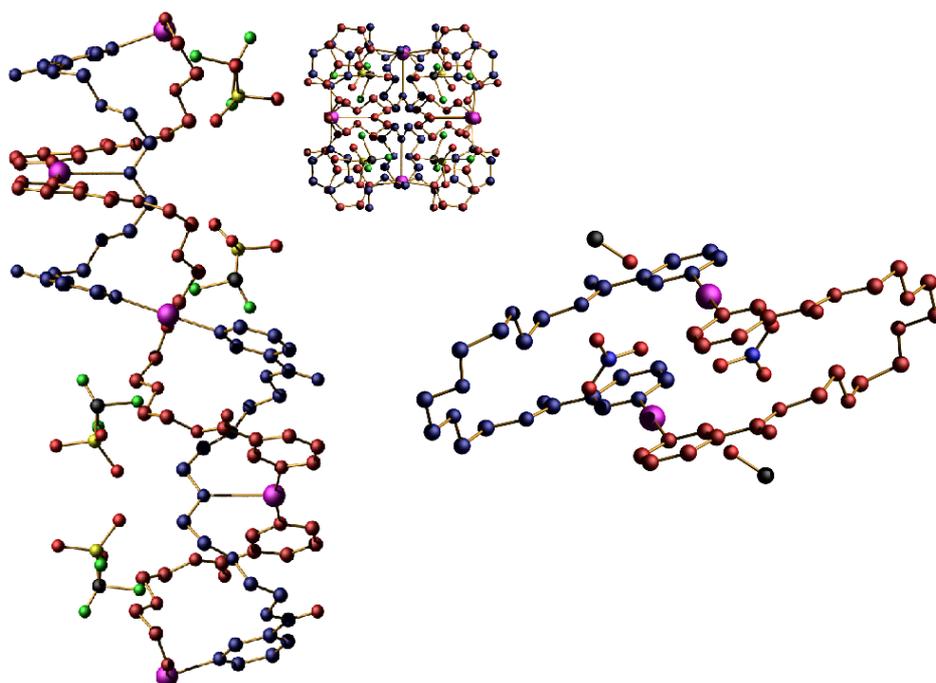
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Complexes with silver ions have a great potential for applications in medical uses. Those complexes with ligands derived from nicotinic acid and with polyethylene oxide groups as spacer are synthesized.

Upon coordination to silver ions, polymorphism can be observed: symmetric or asymmetric metallacycles, single or double helix and, under special conditions, linear chain structures are obtained.



[1] Adeline Y. Robin, Jorge L. Sagué and Katharina M. Fromm, *CrytEngComm*, **8**, 403-416 (2006)

Agenda of the SGK/SSCr General Assembly 2011

September 16, 2011 13.15-13.45h

Freiestrasse 3, Bern

The minutes of our last General Assembly (2010) are published on page 12 and 13 of the SGK/SSCr newsletter No. 81, Dec. 2010, available at <http://www.sgk-sscr.ch/Newsletters/SGK-News-81.pdf>.

- a) Jahresbericht
le rapport annuel
- b) Jahresrechnung
les comptes annuels
- c) Aufstellung des Budgets für das kommende Jahr/
le budget proposé pour l'année suivante
- d) Festsetzung des jährlichen Mitgliederbeitrages/
le montant de la cotisation annuelle
- e) Wahlen/Elections:
 - 1) keine
- f) Anträge von Mitgliedern
 - 1) ECM Conference in Switzerland
The board is proposing a Swiss bidding for the European Conference on Crystallography for 2015 and - in case of rejection – for a re-bidding for 2017
 - 2) other Motions of members

Quorum for final decisions: $\geq 10\%$, out of 166 members = 17 members
(148 regular, 18 students, status August 9, 2011)