

## MS18-O3

## Crystallographic phase transition in single-crystal and powder form, probed by in situ X-ray diffraction under pressure

Elodie Tailleur<sup>1</sup>, Mathieu Marchivie<sup>1</sup>, Patrick Rosa<sup>1</sup>, Jean-Paul Itié<sup>2</sup>, Philippe Guionneau<sup>1</sup>

1. ICMCB-University of Bordeaux, Bordeaux, France
2. Synchrotron SOLEIL, Gif-sur-Yvette, France

email: [tailleur.elo@gmail.com](mailto:tailleur.elo@gmail.com)

Getting **high pressure structural data** still appears a challenging investigation, notably in the field of **molecular materials**. Despite a significant improvement of X-ray diffraction methods and an increasing number of crystal structures under high pressure, **structure-properties relationship** under pressure are rather rare and the microstructural scale is almost unexplored. We have studied a compound having a structural phase transition upon applying pressure whose phases are characterized by different magnetic properties [1]. The present work aims to determine the structural properties under pressure at different scales, from the coordination sphere of the metal center to the crystal packing scale by **in situ Single-Crystal X-Ray Diffraction (SCXRD)** and to correlate them to magnetic properties. Moreover, **in situ high-pressure Powder X-Ray Diffraction (PXRD)** synchrotron experiments have been performed and provide not only an investigation of microstructural properties under pressure but also a fine track of the transition as a function of pressure. In situ PXRD under pressure revealed the behavior of the phase transition including **piezo-hysteresis** [2]. Finally, piezo-hysteresis has been explored by combining high pressure and variable temperature PXRD leading to unexpected behaviors. This work deals with a promising molecular compound with a pressure-induced spin-cross-over at relatively low pressure, about 1.6 kbar, opening potential piezo-switch based applications.

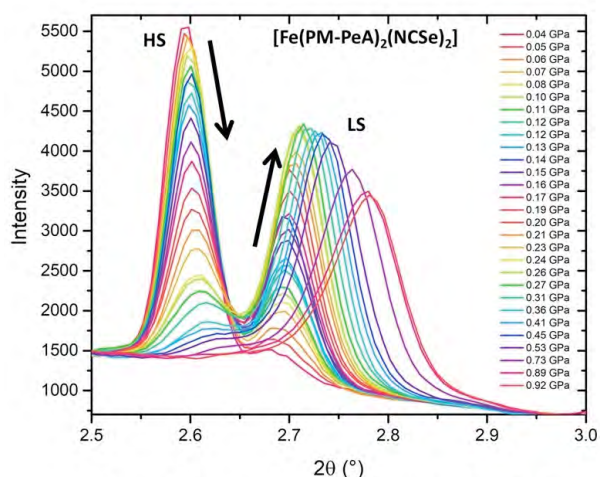


Figure: Pressure-induced Spin-CrossOver shown by the modification of the Bragg peaks intensity

### References:

- [1] E. Tailleur, M. Marchivie, N. Daro, G. Chastanet, P. Guionneau, 2017. Chem. Commun, 53, 4763
- [2] E. Tailleur, M. Marchivie, P. Rosa, J.P. Itié, N. Daro, P. Guionneau, 2018. Angew Chemie. submitted

**Keywords:** Pressure, in situ XRD, Piezo-hysteresis

## MS18-O4

## Penta- and octahedrally coordinated P and Be in high-pressure phases of CaB<sub>2</sub>Si<sub>2</sub>O<sub>8</sub>

Anna Pakhomova<sup>1</sup>, Georgios Aprilis<sup>2</sup>, Maxim Bykov<sup>2</sup>, Liudmila Gorelova<sup>3</sup>, Sergey Krivovichev<sup>3</sup>, Leonid Dubrovinsky<sup>2</sup>

1. Deutsches Elektronen Synchrotron, Hamburg, Germany
2. Bayerisches Geoinstitut, University of Bayreuth, Bayreuth, Germany
3. Saint-Petersburg State University, Saint-Petersburg, Germany

email: [anna.pakhomova@desy.de](mailto:anna.pakhomova@desy.de)

Recent advances in diamond anvil cell techniques combined with third-generation synchrotron facilities enabled *in situ* monitoring of crystal structure evolution up to ultra-high pressures by means of single crystal X-ray diffraction (SCXRD). Recent synchrotron-based experiments have revealed a number of high-pressure polymorphs that are very unusual for the conventional crystal chemistry. One of such examples is danburite, CaB<sub>2</sub>Si<sub>2</sub>O<sub>8</sub>, that follows a step-wise transitions resulting in changes of Si coordination from tetrahedral to octahedral through an exotic trigonal bipyramidal geometry [1]. The discovery of this transformation route has motivated us to investigate the high-pressure behaviour of isotopological mineral hurlbutite, CaBe<sub>2</sub>P<sub>2</sub>O<sub>8</sub>.

SCXRD experiments were performed at the P02.2 beamline at synchrotron Petra III up to 91 GPa. At ambient conditions the crystal structure of hurlbutite (sp. gr. *P2<sub>1</sub>/c*) is built on PO<sub>4</sub> and BeO<sub>4</sub> tetrahedra polymerizing through common vertices with formation of framework featuring four- and eight-membered channels. The 8-membered rings are occupied by Ca atoms. Up to 7.5 GPa conventional continuous contraction of unit-cell parameters is observed. The compression up to 7.5 GPa is controlled by changes in T-O-T angles while the TO<sub>4</sub> tetrahedra stay rigid. Above 7.5 GPa the *b* and *c* axes continue to decrease, while the *a* axis reveals an anomalous increase. This behavior indicates a change in a compression mechanism: half of TO<sub>4</sub> units undergo progressive pressure-induced geometrical distortion. Above 70 GPa the crystal structure undergoes displacive phase transition that is induced by increase of P and one Be coordination number. The new polyhedra of penta-coordinated phosphorus and beryllium possess trigonal bipyramid geometry with two long apical bonds (1.662-1.813 Å for P and 1.711-1.798 Å for Be) and three short equatorial bonds (1.471-1.506 Å for P and 1.492-1.545 Å for Be). Upon further compression above 90 GPa, the appearance of a new phase, co-existing with hurlbutite-II, is observed. The structure of new phase, hurlbutite-III, was solved and refined in the *P-1* space group. All B and P are octahedrally coordinated with P-O bonds of 1.49-1.77 Å and Be-O bonds of 1.50-2.08 Å.

While there are rare reports on existence of P[V] and P[VI] [2,3], the Be[V] and Be[VI] have been not reported before. Hurlbutite-III is the first example of the phase containing the element of the second group in six-fold coordination. The nature of the hypervalent Be-O bonding and the differences between high-pressure routes of danburite and hurlbutite will be discussed.

## References:

- [1] Pakhomova A., Bykova E., Bykov M., Glazyrin K., Biliana Gasharova, Liermann H.P., Mezouar M., Gorelova L., Krivovichev S., Dubrovinsky L. A (2017), *IUCrJ*, 4(5), 671-677.
- [2] Bykov M, Bykova E., Hanfland M., Liermann H.-P., Kremer R., Glaum R., Dubrovinsky L., Smaalen S. (2016) *Angew. Chem. Int. Ed.*, 55(48):15053-15057.
- [3] Pellicer-Porres J., Saitta A.M, Polian A., Itié J.P., Hanfland M, (2007) *Nature Materials* 6, 698-702.

**Keywords:** high-pressure structural analysis; phase transitions; coordination number

**MS18-05**

## Thermal diffuse scattering. A novel approach for probing elasticity at extreme conditions

Bjoern Wehinger<sup>1</sup>, Alessandro Mirone<sup>2</sup>

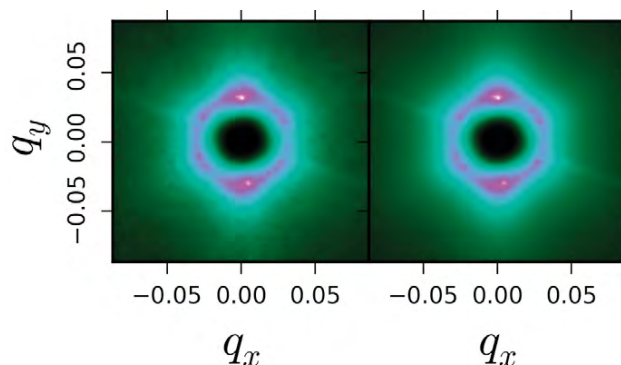
1. Department of Quantum Matter Physics, University of Geneva, Geneva, Switzerland
2. European Synchrotron Radiation Facility, Grenoble, France

**email:** [bjorn.wehinger@unige.ch](mailto:bjorn.wehinger@unige.ch)

I will present a novel and fully quantitative analysis of thermal diffuse x-ray scattering. High-precision measurements of diffuse scattering intensities together with a rigorous data analysis now allow for the determination of the full elasticity tensor in a single crystal diffraction experiment [1], see Figure 1.

Our approach enables a reliable and model-free determination of the elastic properties and can be performed together with crystal structure investigation in the same experiment. Elastic moduli can be extracted from small single crystals of arbitrary symmetry, shape and optical properties and will allow for significant progress in the study of the elastic behaviour of minerals at geophysical relevant conditions, structural phase transitions and fundamental interactions of phonons with other quasi-particles. I will furthermore show that this approach can be applied to high pressure, where the simultaneous measurement of structure and elasticity provides the possibility to establish a primary pressure scale from a single measurement.

Figure 1. Measured (left panel) and calculated (right panel) thermal diffuse scattering from calcite at  $T = 170$  K. The images show a cross-section of the reciprocal space in Cartesian coordinates, in the vicinity of the  $[1, 0, 16]$  reflection. Scattering intensities are shown on a linear color scale from black (zero) to white (maximum intensity).



## References:

- [1] Björn Wehinger, Alessandro Mirone, Michael Krisch and Alexei Bosak, Full Elasticity Tensor from Thermal Diffuse Scattering, *Phys. Rev. Lett.* 118, 035502 (2017). Keywords: diffuse scattering, elasticity

**Keywords:** diffuse scattering, elasticity