

MS18-O3

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

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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.

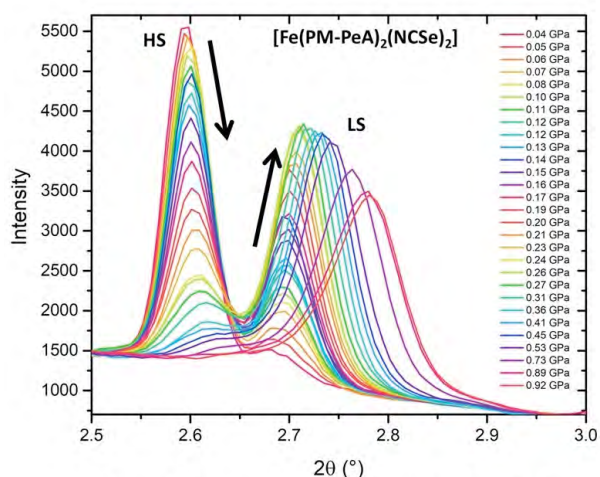


Figure: Pressure-induced Spin-CrossOver shown by the modification of the Bragg peaks intensity

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

MS18-O4

Penta- and octahedrally coordinated P and Be in high-pressure phases of CaB₂Si₂O₈

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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, CaB₂Si₂O₈, 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, CaBe₂P₂O₈.

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. *P2₁/c*) is built on PO₄ and BeO₄ 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 TO₄ 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 TO₄ 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.

Keywords: Pressure, in situ XRD, Piezo-hysteresis