



Past Present *Future*



# GEOMÜNSTER 2019

22–25 September 2019 | Münster | Germany

## Book of Abstracts



Supported by



## 11) Crystallography

### 11a) Structural properties of minerals and materials

Wednesday, 25/Sep/2019: 8:30am - 10:30am

Session Chair: Michael Fischer (University of Bremen)

Session Chair: Thomas Malcherek (Universität Hamburg)

Location: Schlossplatz 7 Hof: SP 7

#### Session Abstract

The characterization of structure, from the atomic level to the micrometer scale, is an important area of overlap between the fields of mineralogy and materials science. This session is intended to bring together researchers from both disciplines. On the one hand, we invite “method-oriented” contributions that focus on the sophisticated application of characterization methods (e.g. X-ray, synchrotron, or neutron diffraction; vibrational spectroscopy; NMR spectroscopy; HRTEM) or of computations (e.g. density functional theory; molecular dynamics) to minerals or synthetic materials. On the other hand, more “materials-oriented” contributions are also very welcome, especially if they aim to enhance the fundamental understanding of material properties (e.g. structure-property relationships), or if they provide new insights that are relevant for technological applications of minerals or materials.

#### Lecture Presentations

8:30am - 9:00am *Session Keynote*

#### **In situ synchrotron studies of open-framework silicates at non-ambient temperature and pressure**

**Paolo Lotti**

*Earth Science Dept., University of Milano, Italy*

The combined use of synchrotron X-ray diffraction (XRD) techniques and devices for *in situ* studies at non-ambient temperature and/or pressure allowed a deep investigation of the behavior of open-framework silicates at these conditions. Displacive phase transitions are common mechanisms adopted by framework compounds to accommodate the bulk expansion or contraction, whenever structural distortion is no more possible or energetically efficient.

The zeolite mordenite, for example, crystallizes, at ambient condition, in the  $Cmc2_1$  space group and undergoes a  $P$ -induced transition to a primitive polymorph. In situ single-crystal synchrotron XRD allowed to identify the space group symmetry ( $Pbn2_1$ ) of the high- $P$  phase and solve its framework structure, allowing to describe the deformation mechanisms triggered by the phase transition at the atomic scale.

In the case of minerals, the fundamental thermo-elastic parameters and their relationship with the crystal structure can be accurately determined. Scapolites are common metamorphic minerals able to accommodate volatiles down to the lower crust, which members represent a complex non-binary solid solution. Modelling the role played by the crystal chemistry on the scapolites behavior is possible by investigating the response of the solid-solution members to  $T$  and  $P$  variations. Our group recently investigated the behavior of an intermediate scapolite (with anomalous  $I4/m$  symmetry) by in situ XRD studies at high- $P$  (ambient- $T$ ), high- $T$  (ambient- $P$ ) and combined high- $T$  and  $P$ , at synchrotron facilities, providing a comprehensive characterization of the elastic and structural response, as well as of a pressure-controlled phase transition to a triclinic polymorph (at  $\sim 9$ -10 GPa) observed at 25 and 650 °C.

In situ synchrotron studies on framework silicates at variable  $P/T$  also allows a better understanding of phe-

nomena, which may be exploited in materials science and technological applications, in particular promoting crystal-fluid interactions at extreme conditions. MFI-zeolites, for example, can be adopted as catalysts in the methanol-to-olefin conversion and pressure may be adopted as a tool to improve the process efficiency, by promoting a larger loading of methanol molecules into the zeolites structural pores. In situ high- $P$  powder XRD experiments on all-silica (silicalite) and slightly cation-exchanged MFI zeolites, using non-penetrating silicone oil and penetrating methanol as  $P$ -fluids, showed a higher efficiency in methanol adsorption by pure silicalite in the lower pressure regime and, conversely, a higher methanol intrusion in cation-exchanged zeolites at  $P > 0.5$  GPa.

**9:00am - 9:15am**

### Crystal Chemistry of the Ion Conducting Li-Oxide Garnet doped with Al, Ga, and Fe

**Georg Amthauer<sup>1</sup>, Daniel Rettenwander<sup>2</sup>, Reinhard Wagner<sup>1</sup>, Günther Redhammer<sup>1</sup>**

<sup>1</sup>University of Salzburg, Department of Chemistry and Physics of Materials, Austria; <sup>2</sup>Institute for Chemistry and Technology of Materials, Graz University of Technology, Austria

#### Crystal chemistry of “Li<sub>7</sub>La<sub>3</sub>Zr<sub>2</sub>O<sub>12</sub>” garnet doped with Al, Ga, and Fe: a review

Recent research has shown that certain Li-oxide garnets with more than 3 Li atoms per formula unit, such as Li<sub>7</sub>La<sub>3</sub>Zr<sub>2</sub>O<sub>12</sub> (LLZO), have high ionic conductivities, as well as good chemical and physical properties for use in solid-state batteries (Murugan et al., 2007).

“Garnet” is the common name for a large number of natural and synthetic metal-oxide phases. Conventional oxide garnets have the general formula A<sub>3</sub>B<sub>2</sub>C<sub>3</sub>O<sub>12</sub> and crystallize in the cubic space group  $la-3d$ . In LLZO the A-positions are occupied by La<sup>3+</sup>, the B-positions by Zr<sup>4+</sup>, and the C-positions by Li<sup>+</sup>. In addition to these cation sites, there are other interstices within the garnet oxygen framework, which are empty in the conventional garnet structure and which are in LLZO filled by “excess” Li<sup>+</sup> ions giving rise to the excellent ionic conductivity.

There is a low temperature tetragonal modification of pure LLZO (SG:  $I4_1/acd$ ) and a high temperature non quenchable cubic phase of LLZO (SG: ). The tetragonal phase has distinctly lower ion conductivity than the cubic phase. Fortunately, the cubic phase can be stabilized at low temperatures by doping with low amounts of Al, Ga, and Fe (Buschmann et al., 2011; Rettenwander et al. 2016). In our contribution the results of single crystal X-ray diffraction studies will be presented. While Al-doped LLZO garnets always crystallize within the space group  $Ga$  and Fe-doped LLZO garnets crystallize within the space group  $I43d$  (Wagner et al., 2016). This symmetry change is combined with an increase in ionic conductivity up to 10<sup>-3</sup> S cm<sup>-1</sup> which is very high for those kind of solid state electrolytes used in Li-ion batteries. These results will be discussed on the basis of the slightly different topologies of both space groups, respectively.

[1] Buschmann H., Dölle J., Berendts S., Kuhn A., Bottke P., Wilkening M., Heitjans P., Senyshyn A., Ehrenberg H. Lotnyk, A. (2011) *Physical Chemistry and Chemical Physics*, 13, 19378-19392; [2] Murugan R., Thangadurai V., Weppner W. (2007). *Angewandte Chemie, International Edition*, 46, 7778-7781; [3] Wagner, R.; Redhammer, G. J.; Rettenwander, D.; Senyshyn, A.; Schmidt, W.; Wilkening, M.; Amthauer, G. (2016). *Chem Mater* 28, 1861-1871; [4] Rettenwander, D.; Redhammer, G.; Preishuber-Pflügl, F.; Cheng, L.; Miara, L.; Wagner, R.; Welzl, A.; Suard, E.; Doeff, M. M.; Wilkening, M.; Fleig, J.; Amthauer G. (2016). *Chem Mater* 28, 2384-2392.

**9:15am - 9:30am**

### Composition dependency of the temperature-driven structural changes in (1-x)PbTiO<sub>3</sub>-xBiNi<sub>0.5</sub>Ti<sub>0.5</sub>O<sub>3</sub>

**Irina Margaritescu<sup>1</sup>, Kaustuv Datta<sup>1</sup>, Jun Chen<sup>2</sup>, Boriana Mihailova<sup>1</sup>**

<sup>1</sup>University of Hamburg, Germany; <sup>2</sup>University of Science and Technology Beijing, China

The (1-x)PbTiO<sub>3</sub>-xBiNi<sub>0.5</sub>Ti<sub>0.5</sub>O<sub>3</sub> (PT-xBNT) perovskite ABO<sub>3</sub> solid solution is a novel ferroelectric material with remarkable piezoelectric properties around the morphotropic phase boundary (MPB) and a high Curie temperature ( $T_C \sim 680$  K at  $x_{MPB} = 0.55$ ). Moreover, PT-xBNT contains a reduced amount of Pb, which makes it an attractive alternative for the current material of choice PbZr<sub>x</sub>Ti<sub>1-x</sub>O<sub>3</sub>. However, the effect of A- and B-site