

Abstract No. jens0329

### Structural Investigation of twinned $\alpha$ -Li<sub>4</sub>Zn(PO<sub>4</sub>)<sub>2</sub>

T. R. Jensen, R. G. Hazell, A. Nørlund Christensen (Dept. of Chem., Univ. of Aarhus, Denmark) and J. C. Hanson (Chem. Dept., BNL).

Beamline(s): X7B

**Introduction:** Hydrothermal preparation techniques have revealed existence of several new lithium zinc phosphates and hydrated zeolite like polymorphs, e.g.  $\delta$ -LiZnPO<sub>4</sub> and  $\beta$ -LiZnPO<sub>4</sub>·H<sub>2</sub>O having a cristobalite related structure and a new variant of the ABW topology, respectively [1,2]. Solid state synthesis and thermal analysis have provided insight in the phase diagram for the system Li<sub>3</sub>PO<sub>4</sub>-Zn<sub>3</sub>(PO<sub>4</sub>)<sub>2</sub> and knowledge of a variety of relatively dense phases, e.g. Li<sub>4</sub>Zn(PO<sub>4</sub>)<sub>2</sub> which exist in two modifications (a reversible phase transition,  $\alpha \leftrightarrow \beta$ , at  $T = 425^\circ\text{C}$  was observed) [3]. A new method for hydrothermal synthesis of  $\alpha$ -Li<sub>4</sub>Zn(PO<sub>4</sub>)<sub>2</sub> is presented providing suitable single crystals for structural investigation.

**Methods and Materials:** Hydrothermal syntheses experiments at temperatures above the critical temperature of water (374°C) were performed in a 2 mL sealed gold ampoule placed in a water-filled 7 mL steel pressure vessel allowing an external water pressure to be applied. The ratio of the reactants were, 7 Li : 1 Zn : 1 PO<sub>4</sub> : 120 H<sub>2</sub>O,  $T = 602^\circ\text{C}$ ,  $p = 1.9 \cdot 10^3$  bar.

**Results:** The single crystals were small (89 × 35 × 35 μm) and twinned so synchrotron X-ray radiation was necessary to provide sufficient information on the weak reflections. The wavelength was,  $\lambda = 0.9346(1)$  Å and the data collection temperature was,  $T = 25(2)^\circ\text{C}$ . If the two twins are equally strong, apparent perfect orthorhombic symmetry (previously suggested space group  $C222_1$  [3]) is obtained and would cause serious difficulties finding a structural model. In this case the ratio between the two twins was ca. 40/60 and the new space group was  $P2_1/a$  ( $R(F) = 0.042$ ). The cations are coordinated to four oxygens each. The Figure visualize the crystal structure of  $\alpha$ -Li<sub>4</sub>Zn(PO<sub>4</sub>)<sub>2</sub> as polyhedra (P and Zn) and with Li shown as atoms. The (101) projection reveals 4-rings and apparent 8 rings of PO<sub>4</sub> and ZnO<sub>4</sub> tetrahedra. It turns out that the structure of  $\alpha$ -Li<sub>4</sub>Zn(PO<sub>4</sub>)<sub>2</sub> is related to the structure of  $\gamma$ -Li<sub>3</sub>PO<sub>4</sub>. The virtual substitution of  $\text{Li}^+ \rightarrow 1/2\text{Zn}^{2+}$  transforms  $\gamma$ -Li<sub>3</sub>PO<sub>4</sub> to  $\alpha$ -Li<sub>4</sub>Zn(PO<sub>4</sub>)<sub>2</sub> and substitution of  $2\text{Li}^+ \rightarrow \text{Zn}^{2+}$  to  $\delta$ -LiZnPO<sub>4</sub> [4].

**Acknowledgments:** The work at BNL was supported by contract DE-AC02-98CH10086 with the US DOE Div. of Chemical Sciences and the Danish National Research Council (Dansync).

**References:** [1] T. R. Jensen, P. Norby, P. C. Stein and A. M. T. Bell, *J. Solid State Chem.* **117**, 39 (1995). [2] T. R. Jensen, *J. Chem. Soc., Dalton Trans.* 2261 (1998). [3] G. Torres-Trevino and A. R. West, *J. Solid State Chem.* **61**, 56 (1986). [4] T. R. Jensen, R. G. Hazell, A. Nørlund Christensen and J. C. Hanson, *J. Solid State Chem.*, **166**, 341-351 (2002).

