A new ionic conductor compound, $(Li, Na, H)_{0.16}Zn_{1.92}SiO_4$

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Using X-ray single crystal (XRD) diffraction data at F1 (DORIS) in combination with high-resolution neutron powder diffraction (HRNPD) at SPODI (FRMII) we could report about the presence of Li^+, Na^+, and H^+ cations in four and six membered-ring channels in a new willemite-type compound, [$(Li, Na, H)_{0.16}Zn_{1.92}SiO_4$)] (Fig. 1). This material stable at least up to 1000 °C shows high static and dynamic cationic motions can be a prototype for combined cationic conductors (Fig. 2).

High-temperature XRD study is the main contribution on this study, so that we report here the experiment part on a kappa four-circle single crystal diffractometer at the beam line F1 (DORIS). The details of the structure elucidation are the extended report published in 2013 [1]: A needle-like crystal (5 x 11 x 300 μm^3) was mounted on a 0.3 mm silica glass capillary using ZrO_2-paste. A short wavelength of 0.5600(3) Å was chosen to cover high ($\sin\theta / \lambda$)-ranges (up to 1.41). Integrated intensities were measured with a step size of 1° (φ) per frame using a charge-coupled detector (MarCCD165) positioned at 80 mm from the crystal. A data collection strategy with three different combinations of Eulerian angles for each temperature was chosen: 1. Run at $2\theta = 0°$, $\omega = 0°$, $\chi = 0°$ with 40 sec/frame; 2. Run at $2\theta = -60°$, $\omega = 0°$, $\chi = 0°$ with 180 sec/frame; 3. Run at $2\theta = -60°$, $\omega = 20°$, $\chi = 60°$ with 180 sec/frame. At 800°C the exposure time was increased by 20 sec for all frames. A N_2 gas stream heating device was calibrated manually for a temperature range of 20 - 900 °C, and data collections were carried out at 20, 300, 600, and 800 °C.

References

1. S.-H. Park, C. J. Chucholowski, L. Garcia B. Lara, M. Hoelzel, C. Paulmann, *"Investigation of a new willemite-type compound, $(Li, Na, H)_{0.16}Zn_{1.92}SiO_4$"*, J. Solid St. Chem. **200** (2013), 328-340.

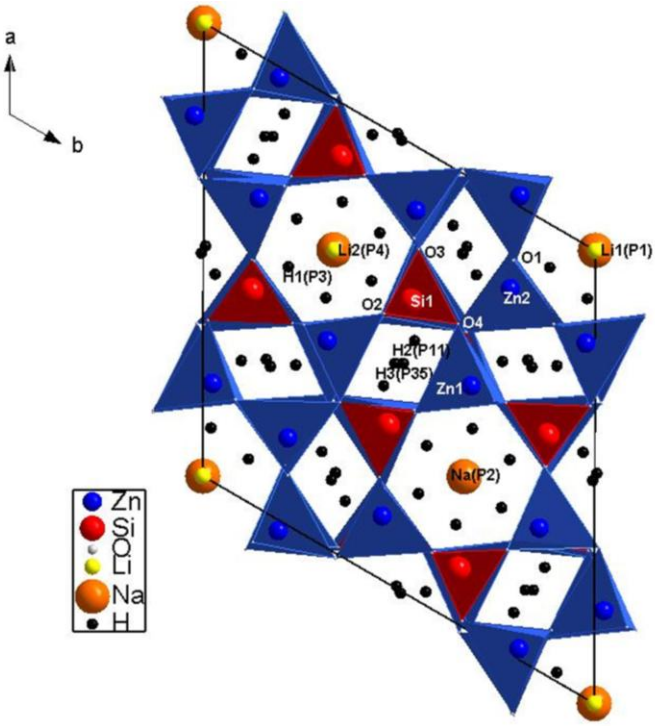

Figure 1: Structure model for the refined framework of (Li, Na, H)-willemite parallel to the *c*-axis. Li and Na cations occupy the sites Li1, Li2, and Na which are arranged parallel to the *c*-axis around the center of 6MR-channels. Protons seem to be sited in both 6-/4MR-channels.

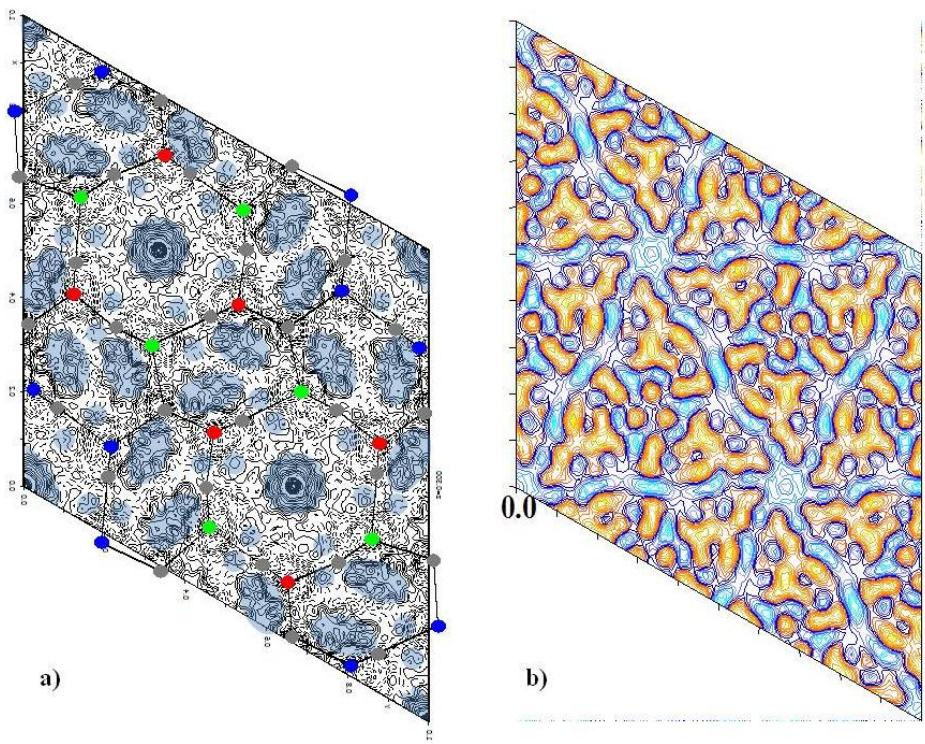

Figure 2: Difference Fourier (ΔF) maps evaluated with XSD (a) and HRNPD data (b) at 20 °C. Respective density of electrons (a) and neutron scattering lengths (nsl) (b) are summed up for z from 0 to 1 and plotted at z = 0.5, where positive (continuous lines) and negative (broken lines) electron densities are contoured between 0.6 and -0.5 [e $Å^{-3}$]; positive (reddish) and negative (pale blue) nsl densities are mapped between 0.1 and -0.1 [coh *b* $Å^{-3}$]. Relatively strong negative nsl densities presented in 2b are sited at the same locations where strong positive electron densities are found in 2a (hatched regions). The framework Si, Zn, and O atoms are indicated as red, green, and grey circles in 2a.