High-temperature Neutron Diffraction of $Li_{1.2}Al_{0.2}Ti_{1.8}P_3O_{12}$

Enkhtsetseg Dashjav,[1] *Raphael Hermann,* [2] *Frank Tietz* [1]

[1] Institute of Energy and Climate Research (IEK), Forschungszentrum Jülich GmbH, D-52425 Jülich, Germany
[2] Jülich Centre for Neutron Science (JCNS) and Peter Grünberg Institut (PGI), Forschungszentrum, JARA-FIT, Forschungszentrum Jülich GmbH, D-52425 Jülich, Germany; Faculté des Sciences, University of Liège, B-4000 Liège, Belgium

Corresponding author: Dr. Frank Tietz, E-Mail: f.tietz@fz-juelich.de

The crystal structure of the Li^+ ion-conducting material $Li_{1.2}Al_{0.2}Ti_{1.8}P_3O_{12}$ (LATP) was investigated by X-ray and neutron powder diffraction between 25 and 850 °C in order to elucidate the temperature-dependent distribution of Li^+ ions and to identify possible paths of ionic migration. The crystal structure is thermally stable up to 1000 °C and retains its NASICON-type crystal structure throughout the studied temperature range. The unit cell volume of LATP increases nearly linearly with increasing temperature up to about 500°C. At 550-650 °C and 750-800 °C two changes of slope in the cell volume are observed (Fig. 1), which seem to correlate with an enhanced ionic migration in the structure. The thermal expansion behavior of a LATP ceramic sample shows a different curve than the cell volume (Fig. 1) with an increased slope from 450 °C and a shrinkage starting at 720 °C due to creep of the sample induced by the pressure of the push rod of the dilatometer. The above mentioned temperature ranges for structural changes are in good agreement with irregularities of conductivity data (Fig. 2). Except for Li atoms, all atomic displacement parameters (ADP) increase only slightly up to 850 °C. The ADP of Li atoms increase stronger at T > 300 °C and then show a decreasing slope at 600 °C. This is comparable with results of $LiZr_2(PO_4)_3$ showing a transition temperature from normal to superionic conductor at about 330 °C [1]. Previous neutron diffraction investigations on LATP identified a trigonal prismatic 6a site for excess Li^+ ions [2]. In this study, however, additional disorder of excess Li^+ ions was observed at room temperature, occupying split sites at 36*f* (0.2626 0.8894 0.0855).

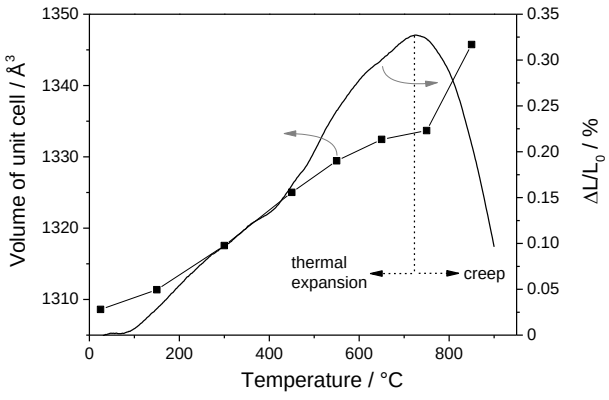

Figure 1: Unit cell volume and thermal expansion of LATP as a function of temperature

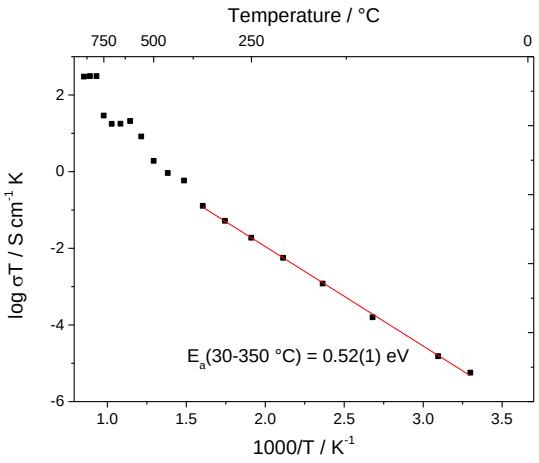

Figure 2: Arrhenius plot of ionic conductivity of LATP

The Spallation Neutron Source and C. M. N. Kumar are acknowledged for provision of and assistance during neutron beam time at POWGEN.

References

[1] P. Padma Kumar, S. Yashonath, *J. Phys. Chem. B* 2001, ***105***, 6785-6791.
[2] E. Dashjav, F. Tietz, *ZAAC* in print.