

MS19-P9 Crystal structure, microstructure and ionic conductivity of the cost-efficient sodium solid electrolyte $\text{Na}_3\text{YSi}_4\text{O}_{12}$

Wolfram Münchgesang¹, Dörte Wagner², Mykhaylo Motylenko³, Ulrike Langklotz², Tina Nestler¹, Anastasia Vyalikh¹, Falk Meutzner¹, Axel Rost², Jochen Schilm², Tilmann Leisegang^{1,4}, Vladislav A. Blatov⁴, David Rafaja², Dirk C. Meyer¹

1. Technische Universität Bergakademie Freiberg, Institut für Experimentelle Physik, Leipziger Straße 23, 09596 Freiberg, Germany
2. Fraunhofer Institute for Ceramic Technologies and Systems IKTS, Winterbergstraße 28, 01277 Dresden, Germany
3. Technische Universität Bergakademie Freiberg, Institute of Materials Science, Gustav-Zeuner-Straße 5, 09596 Freiberg, Germany
4. Samara State Aerospace University, Samara Center for Theoretical Materials Science, Moskovskoye Shosse 34, Samara 443086, Russia

email: Wolfram.muenchgesang@physik.tu-freiberg.de

There exist a number of solid-electrolyte materials for sodium battery technologies characterized by intermediate complexity of the corresponding crystal structures. Beside the well-known sodium solid-electrolytes, β^{++} -alumina and NASICON, $\text{Na}_3\text{YSi}_4\text{O}_{12}$ is another promising phase with a high ionic conductivity. Its main advantage over the two above-mentioned structures is a lower production complexity and thus associated costs. However, very little is known about the correlation between the complex crystal structure, with their one-dimensional ion migration pathways, the microstructure and the interplay with Na^+ ionic conductivity.

In this work, the phase content, the phase distribution, the migration pathways and the ionic conductivity of polycrystalline $\text{Na}_3\text{YSi}_4\text{O}_{12}$ -based materials, obtained by a glass-ceramic process, have been analyzed by means of X-ray powder diffraction, scanning electron microscopy, solid-state nuclear magnetic resonance and electrical impedance spectroscopy. These experimental results were discussed with respect to theoretical considerations of the crystal structure, based on the bond valence method and the Voronoi-Dirichlet approach, and other Na^+ conductors.

This work was financially supported by the BMWi within the project BaSta (0325563D) and the BMBF within the projects CryPhysConcept (03EK3029A) and SyNeSteSia (05K2014).

Keywords: ionic conductivity, solid electrolyte, ceramic, bond valence, Structure conductivity correlation

MS19-P10 Experimental visualization of the Na diffusion paths in $\text{Na}_{0.7}\text{CoO}_2$, a prospective cathode material for Na-ion batteries

Marisa Medarde¹, Medarde Marisa¹, Mena Mattia², Gavilano Jorge², Pomjakushina Ekaterina¹, Kamazawa K³, Pomjakushin Vladimír², Sheptyakov Denis², Batlogg Bertram¹, Ott Hans-Rudolf⁴, Månsson Martin⁵, Juranyi Fanni²

1. Laboratory for Scientific Developments and Novel Materials, Paul Scherrer Institut, 5232 Villigen PSI, Switzerland
2. Laboratory for Neutron Scattering and Imaging, Paul Scherrer Institut, CH-5232 Villigen PSI, Switzerland
3. Comprehensive Research Organization for Science and Society (CROSS), Tokai, Ibaragi 319-1106, Japan
4. Laboratory for Solid State Physics, ETH Zürich, CH-8093 Zürich, Switzerland
5. KTH Royal Institute of Technology, SE-100 44, Stockholm, Sweden

email: marisa.medarde@psi.ch

The layered cobaltite Na CoO_2 ($0 < x < 1$) has been extensively studied during the last decade due to the unusual evolution of its electronic and magnetic properties with the Na content (and hence the $\text{Co}^{3+}/\text{Co}^{4+}$ ratio). Its phase diagram includes metallic and insulating phases, charge order, frustrated magnetism, and even a small region where superconductivity appears when H_2O molecules are intercalated between the CoO_2 layers. Interestingly, this material has also attracted the attention of applied sciences due to its structural similarity with Li_xCoO_2 , which is one of the most common electrode materials in Li-ion batteries. In view of the larger abundance of Na in the earth crust with respect to Li and the increasing interest on cheaper Na-ion batteries for grid storage, we have investigated the Na-ion diffusion in Na CoO_2 by means of NMR¹, μSR ², elastic³ and quasielastic⁴ neutron scattering in order to assess the use of this material as cathode for solid-state rechargeable batteries.

For this purpose we choose the material with $x=0.7$, where the tendency of Na ions to form ordered superstructures might reduce the ionic conductivity. By combining these techniques we could establish the existence two structural transitions at $T_1=290\text{K}$ and $T_2=400\text{K}$. Analyses of the anomalies in the Na-Na distances, the Debye-Waller factors and the scattering density in the paths connecting neighbouring Na sites unambiguously showed that both transitions are related to changes in the Na-ion mobility. Moreover, we found that ionic diffusion in this material occurs through the successive opening of first quasi-1D ($T_1 < T < T_2$) and then 2D ($T > T_2$) Na diffusion paths within the Na layers³. These findings provide new insight on the subtle mechanisms controlling the Na-ion diffusion in the Na CoO_2 series and indicate that even in the less favourable member of the family ion diffusion is already present at RT.

¹ Weller et al., PRL **102**, 056401 (2009)

² M. Månsson et al., Phys. Scr. **88** (2013) 068509

³ M. Medarde et al., PRL **110** (2013) 266401

⁴ F. Juranyi et al., EPJ Web Confs. **83** (2015) 02008