

Conduction Pathways in Alkali Lanthanide Pyrosilicates, $A_3LnSi_2O_7$

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Sodium and lithium ion conductors with good electrochemical stability and ion mobility are of interest as solid electrolytes, a key component in all solid state batteries. Crystalline solid electrolytes are characterised by a host framework of immobile ions with a sublattice of mobile species connected via conduction pathways forming a percolating network¹. The $A_3LnSi_2O_7$ (A = alkali metal; Ln = lanthanide) type structure is a good candidate for alkali ion conduction because it has sufficient free volume between nearest-neighbour alkali ion sites to support a percolating network (Fig. 1). Moreover, the versatility of the alkali lanthanide pyrosilicate framework ($A_3LnSi_2O_7$) allows for the crystal structure to support a homologous series of alkali-metal and lanthanide ions. Previous studies have characterised $Na_3LnSi_2O_7$ (Ln = Ho, Y, Tm-Sc) and $K_3LnSi_2O_7$ (Ln = Sm-Lu)³⁻⁶. Only a single publication reports the sodium-ion conductivity of polycrystalline $Na_3LnSi_2O_7$ (Ln = Y, Gd) with no analysis of conduction mechanisms, and the structure of Li-containing $Li_3LnSi_2O_7$ has not yet been reported.

In this poster, the synthesis of $A_3LnSi_2O_7$, (A = Na, K; Ln = Gd-Lu) by the solid state method, and metastable $Li_3LnSi_2O_7$ by a molten salt ion exchange, will be described. Structural analysis of the $A_3LnSi_2O_7$ compounds by powder X-ray and neutron diffraction will be discussed and a comparison drawn between their average structures. Neutron total scattering measurements and ²³Na solid state NMR techniques will be used to elucidate their local structure and gain insight into the dynamics of the alkali ion. Ionic conductivity measurements by electrochemical impedance spectroscopy (Fig. 2) will be used to compare the alkali ion mobility. Finally, predictions of potential diffusion pathways informed by local structural models, bond valence sum difference maps, and DFT calculations will be presented.

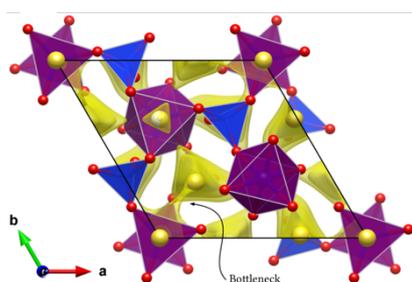


Figure 1: The $A_3LnSi_2O_7$ crystal structure (top inset) is shown with A^+ (atoms, bonds not shown), O^{2-} (atoms), Ln^{3+} (octahedra), Si^{4+} (tetrahedra), and a bond valence sum difference map, calculated with the softBV parameters², shown with an isosurface level of 0.08.

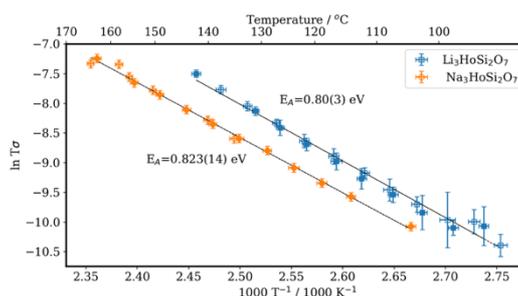


Figure 2: Arrhenius plot of the ionic conductivities measured by impedance spectroscopy for pellets of $Li_3HoSi_2O_7$ (squares) and $Na_3HoSi_2O_7$ (diamonds). Filled points were collected during heating and open points during cooling.

References:

- [1] Adams, S. *Solid State Ionics* **177**, 1625–1630 (2006)
- [2] Latshaw, A. M., et al. *J. Solid State Chem.* **235**, 100–106 (2016)
- [3] G.R. Mettam, L.B. Adams, in: B.S. Jones, R.Z. Smith (Eds.), *Introduction to the Electronic Age*, E-Publishing, Inc. New York, 2009, pp. 281–304.