Experimental report

02/12/2021

Proposal: 5-21-1164 **Council:** 10/2020

Title: Structure Determination of High Entropy Lithium Argyrodite SuperionicConductors

Research area: Chemistry

This proposal is a new proposal

Main proposer: Florian STRAUSS

Experimental team: Clemens RITTER

Local contacts: Clemens RITTER
Claire COLIN

Samples: Li6PS5[Cl0.33Br0.33I0.33]
Li6PS2.5Se2.5[Cl0.33Br0.33I0.33]
Li6.5[Ge0.5P0.5]Se5[Cl0.33Br0.33I0.33]
Li6.67[Si0.33Ge0.33P0.33]S2.5Se2.5[Cl0.33Br0.33I0.33]
Li6PSe5[Cl0.33Br0.33I0.33]
Li6.67[Si0.33Ge0.33P0.33]S5[Cl0.33Br0.33I0.33]
Li6.67[Si0.33Ge0.33P0.33]Se5[Cl0.33Br0.33I0.33]
Li6.5[Ge0.5P0.5]S5[Cl0.33Br0.33I0.33]
Li6.5[Ge0.5P0.5][S2.5Se2.5[Cl0.33Br0.33I0.33]

Instrument	Requested days	Allocated days	From	To
D2B	0	2	31/05/2021	02/06/2021
D1B	2	0		

Abstract:

High entropy stabilized materials and lithium superionic conductors are currently attracting tremendous research interest due to their unprecedent physical/chemical properties and enabler for solid state batteries respectively. In the present proposal, the concept of configurational high entropy, so far demonstrated for alloys and recently applied to ceramics is transferred to argyrodite-type Li-ion conductors by introducing high entropy via simultaneously introducing equimolar amounts of cations well as anionic species while maintaining the original crystal structure. For instance, Li6.67[Si0.33Ge0.33P0.33[]S2.5Se2.5][Cl0.33Br0.33I0.33] has been successfully prepared throughout the preliminary work, showing promising Li-ionic conductivity (> 3 mS/cm). However using X-ray diffraction it is impossible to exactly determine the Li positions/occupancies, necessary to understand Li-ion conduction in such materials. Thus, neutron diffraction is inevitable to fully solve the crystal structure of such novel high entropy superionic lithium conductors.

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The experiments were conducted by the local contact without any members of the proposal due to the COVID-19 pandemic.

Neutron diffraction measurements were carried out at room temperature for 6 samples. However there was an amendment to the compositions described in the original proposal due to difficulties to synthesize these materials in the desired amount and purity. Instead related $Li_{6.5}[Si_{0.25}Ge_{0.25}P_{0.25}Sb_{0.25}]S_5I$ (quenched), $Li_{6.5}[Si_{0.25}Ge_{0.25}P_{0.25}Sb_{0.25}]S_5I$ (naturally cooled) $Li_{6.5}[Si_{0.25}Ge_{0.25}P_{0.25}Sb_{0.25}]S_5I$ (slow cooled), $Li_{6.5}[Si_{0.2}Ge_{0.2}Sn_{0.2}P_{0.2}Sb_{0.2}]S_5I$ and Li_4PS_4I (quenched and naturally cooled) were measured. Powdered samples were sealed in vanadium cylinders at the Karlsruhe Institute of Technology (KIT) and send to the local contact. For the three $Li_{6.5}[Si_{0.25}Ge_{0.25}P_{0.25}Sb_{0.25}]S_5I$ samples and for one Li_4PS_4I diffraction measurements were also conducted at 10 K as suggested by the local contact to get more detailed information about the Li substructure. Each sample was measured for about 5.5 h. However for the $Li_{6.5}[Si_{0.2}Ge_{0.2}Sn_{0.2}P_{0.2}Sb_{0.2}]S_5I$ sample, the measurement was aborted after about 2.75 h as the diffraction was very poor most likely due to the presence of a large amorphous fraction within the sample.

Currently all data are analyzed via Rietveld refinement. The data obtained from this experiment will be part of a PhD thesis and furthermore published in peer-reviewed journals in combination with complementary physical property measurements.