Experimental report

16/09/2022

Proposal: 5-23-773 **Council:** 4/2021

Title: Assessing the influence of Li+ carrier density and Li+ substructure on ionic conductivity of substitutedhalide spinel Li2+xSc2/3-xMgxCl4

Research area: Materials

This proposal is a new proposal

Main proposer: Wolfgang ZEIER

Experimental team:

Local contacts: Emmanuelle SUARD

Samples:
Li2.42Sc0.25Mg0.42Cl4
Li2.14Sc0.53Mg0.14Cl4
Li2Sc2/3Cl4
Li2.63Sc0.04Mg0.63Cl4
Li2.07Sc0.6Mg0.07Cl4
Li2.49Sc0.18Mg0.49Cl4
Li2.56Sc0.11Mg0.56Cl4
Li2.28Sc0.39Mg0.28Cl4
Li2.21Sc0.46Mg0.21Cl4
Li2.35Sc0.32Mg0.35Cl4
Li2.66Mg2/3Cl4

Instrument	Requested days	Allocated days	From	To
D2B	2	1	27/09/2021	28/09/2021

Abstract:

Lithium conducting halide spinels got back into focus of solid electrolyte researchers when Li2Sc2/3Cl4 was rediscovered exhibiting three-dimensional diffusion pathways and a high room-temperature conductivity of 1.5 mS·cm-1. Within these halide spinels, the Li+ carrier density was tuned by metal ion self-doping introducing vacancies. Incorporation of external dopants is rarely known, hence the effects of aliovalent substitution is one of the prime focus to understand the effect of lithium substructure on the transport properties of halide electrolytes. In this proposed experiment, we want to investigate the Li2+xSc2/3-xMgxCl4 substitution series in terms of structure-property relationships to assess the influence of the Li+ substructure on the ionic conductivity as well as the overall impact of Mg2+ substitution.

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The temperature dependence of phase formation in $Li_2Sc_{2/3}Cl_4$ – additional measurement to the Proposal 5-24-664

Within this beamtime, additional temperature-dependent measurements were performed to complete the data set of the proposal 5-24-664. The low temperature data should aid to solve the structure for the different annealing temperatures by revealing atoms on crystallographic positions which have lower relative site energies compared to the other sites. For this temperature-dependent study, the sample annealed at 450 °C with the highest content of monoclinic phase (around 80 %) and the sample annealed at 750 °C with an almost 50:50 wt.% mixture were investigated.

The Li-Sc-Cl samples were synthesized mechanochemically by using the precursors LiCl and $ScCl_3$ in stoichiometric amounts. Subsequently, the samples were annealed at 450 °C and 750 °C for 30 min and directly air-quenched. The obtained powder were hand ground for further analysis including neutron diffraction studies. The neutron powder diffraction data were recorded at 100 K, 150 K, 200 K and 250 K for the 450 °C sample and at 100 K and 150 K for the 750 °C sample. Room-temperature data was already recorded within the proposal 5-24-664. All measurements were carried out at the D2B high-resolution powder diffractometer at the Institute Laue-Langevin beamline (ILL, Grenoble, France) with a monochromatic (Ge(335)) neutron wavelength $\lambda = 1.594$ Å in a range of $2\theta = 0 – 160°$ with 0.05 steps for 4 hours.

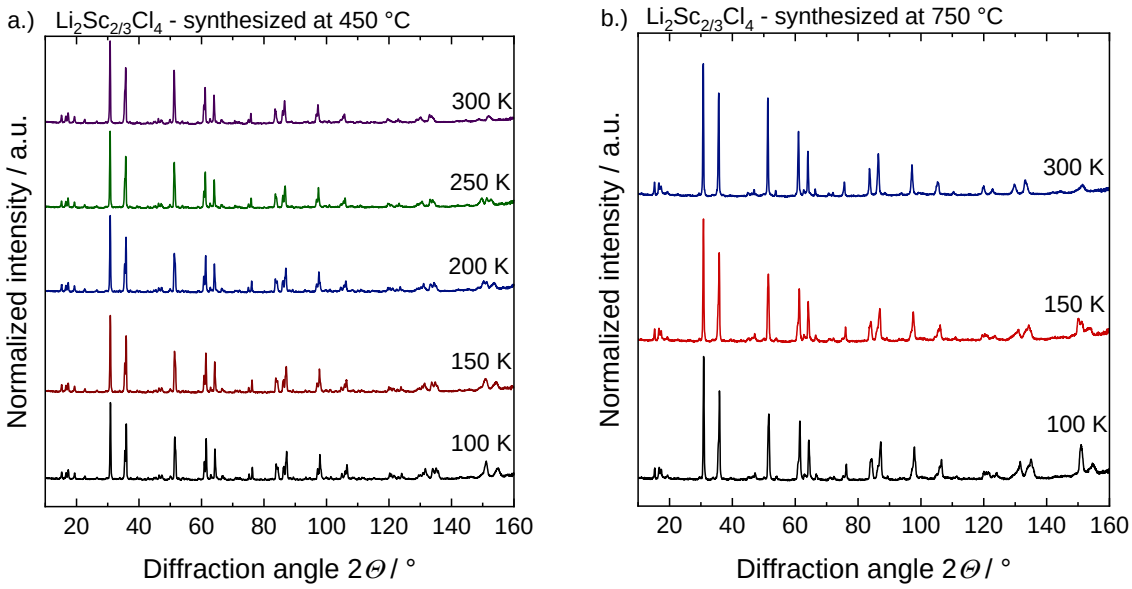

Figure 1: Stacked neutron powder diffraction pattern of the Li-Sc-Cl samples a.) synthesized at 450°C measured at 100 K, 150 K, 200 K, 250 K and 300 K and b.) synthesized at 750°C measured at 100 K, 150 K and 300 K.

The intention of the temperature-dependent diffraction study was to reveal the most stable configuration for each crystal structure, since cooling freezes the atomic-motion. Several high-angle reflections change indicating that within smaller *d*-spacings the structure changes, see figure 1 a.) and b.). The refinement of low temperature (100 K) neutron powder diffraction data of the 450 °C sample indicates a major

amount of monoclinic phase in the composition, see figure 2 a.). This is in accordance with the room-temperature data of the 450 °C data showing the highest amount of monoclinic phase (see proposal 5-24-664). A two-phase refinement using the monoclinic and the cubic phase (figure 2 b.) lead to a fraction of roughly 15 wt.-% of cubic phase, still leaving the question open, if a phase mixture is present or the sample has stacking fault like previously reported ternary halides in similar structure (*Chem. Mater.* **2022**, *34*, 3227−3235).

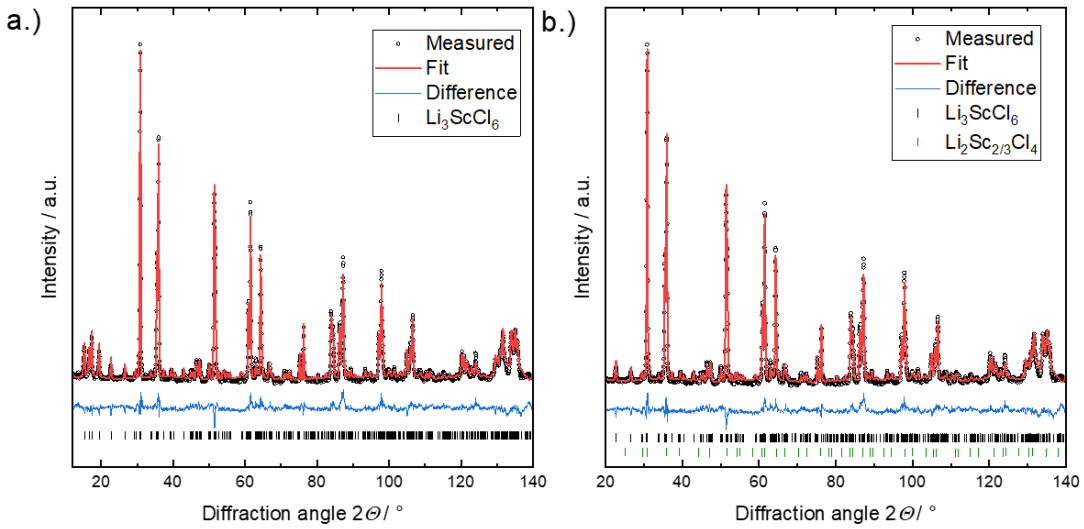

Figure 2: Rietveld refinement of the 450 °C sample at 100 K with a.) only monoclinic phase and b.) monoclinic and cubic phase.

Additional X-ray pair distribution function measurements at room-temperature show that the two samples exhibit similar behavior (see figure 3), there are minor differences in the distances at low angle region, which now will be further analyzed using synchrotron diffraction to understand the influence of annealing temperature on the structure. The differences at low *d*-spacing can indicate differences in the bonding interaction and we try to correlate these, then with the neutron data in a coupled refinement. Overall, these similar atomic distances in the two samples leave in the dark whether stacking faults or a phase change happens. We are in contact with a group that already refined the stacking faults in halide-based samples to fully understand the Li-Sc-Cl system and try to solve the structures (literature: *Chem. Mater.* **2022**, *34*, 3227−3235, *J. Am. Chem. Soc*. **2022**, *144*, 5795−5811).

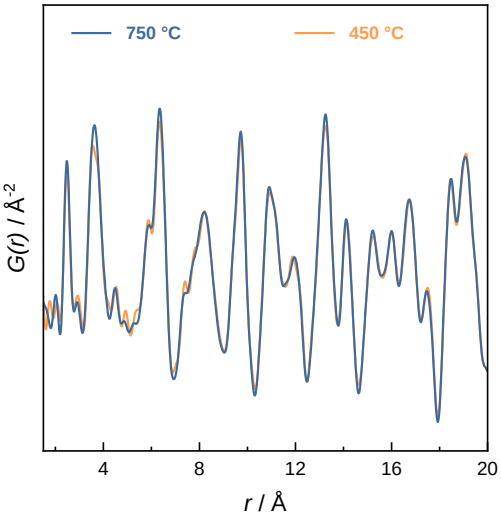

Figure 3: Fourier transformed PDF data of the two samples annealed at 450 °C (yellow) and 750 °C (blue). The two samples show differences in the low atomic distance up to 6 Å.