Experimental report

27/06/2022

Proposal:	**5-24-664**	**Council:**	10/2020

Title: Unravelling the structure-transport correlations in $Li_{3-x}In_{1-x}Zr_xCl_6$

Research area: Materials

This proposal is a new proposal

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Samples: $Li_{2.9}In_{0.9}Zr_{0.1}Cl_6$
$Li_{2.7}In_{0.7}Zr_{0.3}Cl_6$
Li_3InCl_6
$Li_{2.8}In_{0.8}Zr_{0.2}Cl_6$
$Li_{2.6}In_{0.6}Zr_{0.4}Cl_6$
$Li_{2.5}In_{0.5}Zr_{0.5}Cl_6$
Li, Sc, Cl element and $Li_2Sc_{2/3}Cl_4$ (Total sample 5)
Li, Sc, Mg, Cl element and $Li_{2+x}Sc_{2/3-X}Mg_xCl_4$ (Total sample 3)
Li, Sc, Zr, Cl element and $Li_{2-x}Sc_{2/3-x}Zr_xCl_4$ (Total sample 3)

Instrument	Requested days	Allocated days	From	To
D2B	3	3	09/07/2021	12/07/2021

Abstract:

The rare-earth halides Li_3MX_6 (M = Y, Er, In; X = Cl, Br, I) show promising high potential electrochemical stabilities and ionic conductivities in the mS/cm range, which is comparable to the lithium thiophosphates. Currently, the knowledge about the impact of isovalent or aliovalent substitutions within these compounds is very limited, which is usually a very well-known strategy to tune the ionic transport properties. In preliminary data, we observed a significant enhancement in ionic conductivity of Li_3InCl_6 substituting In with Zr which needs further investigation. Therefore, we propose neutron diffraction experiments in the series of solid solutions $Li_{3-x}In_{1-x}Zr_xCl_6$ (x = 0-0.5) to correlate the structural impact of the Zr-substitution with the transport behaviour in order to determine the Li substructure and find structure-property relationships.

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1.) The temperature dependence of phase formation in $Li_2Sc_{2/3}Cl_4$

Halide-based material like Li_3MX_6 (M = metal, X = halide) have garnered attention as promising candidates for solid electrolytes in the last years. The high conducting rare-earth metal halides usually crystallize in a monoclinic or trigonal phase. Among them, lithium ion conducting ternary scandium halide has been studied extensively due to their high conductivity and structural diversity. The disordered spinel $Li_2Sc_{2/3}Cl_4$ shows high conductivities in the $mS \cdot cm^{-1}$ range and can be synthesized via solid-state synthesis at 650 °C (*Energy Environ. Sci.*, **2020**, *13*, 2056). Furthermore, the monoclinic Li_3ScCl_6 is also synthesized in a solid-state synthesis at 650 °C, but with longer annealing duration and a specific cooling rate (*J. Am. Chem. Soc.*, **2020**, *142*, 7012−7022). The stoichiometry of $Li_2Sc_{2/3}Cl_4$ comes up to Li_3ScCl_6 when multiplying with 1.5. At this point, it is important to study the effects of synthesis on the formation preference of the competing monoclinic and cubic phase.

The Li-Sc-Cl samples were synthesized via ball-milling by using the precursors LiCl and $ScCl_3$ in stoichiometric amounts. Subsequently, the compounds were annealed at different temperatures of 450 °C, 550 °C, 600 °C, 650 °C and 750 °C for 30 min and directly air-quenched. The obtained powders were hand ground for further analysis including neutron diffraction studies. All neutron powder diffraction data were measured at room-temperature on 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. Measured X-ray diffractograms suggest a phase transition at around 600 °C from monoclinic to cubic. Due to the low X-ray scattering form factor of lithium ions no detection of the different lithium substructures can be revealed with this method.

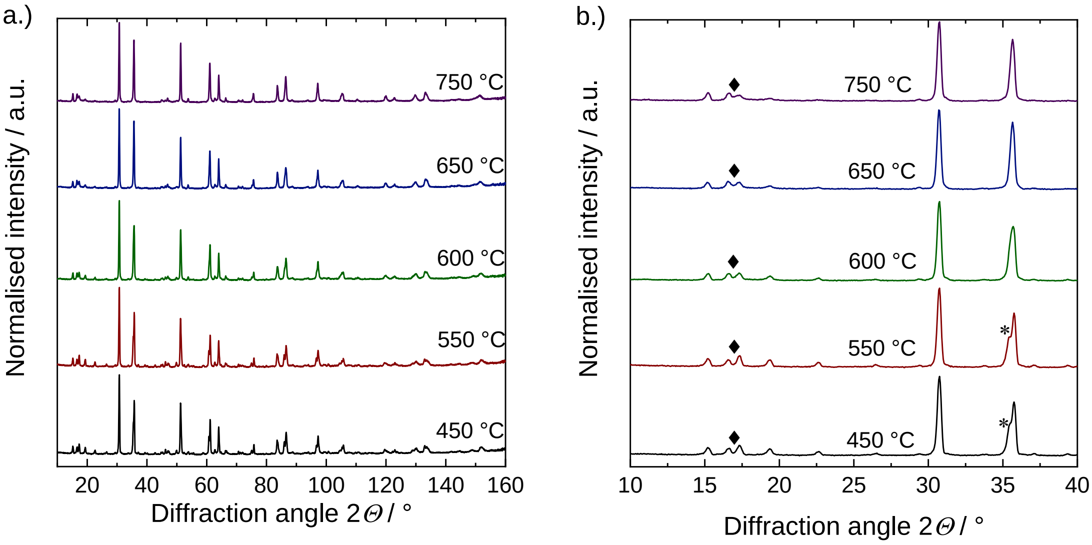

Figure 1: a.) Stacked neutron powder diffraction pattern of the Li-Sc-Cl samples synthesized at different temperatures and b.) diffraction angle range of $2\theta = 10 - 40$ ° with marked differences in the reflections over the different temperatures.

Figure 1 shows the measured neutron powder diffraction pattern of different annealing times. Preliminary refinements of the neutron data using the Software TOPAS-Academic V6 software package indicated a phase mixture of the monoclinic and cubic phase of the Li-Sc-Cl samples for different temperatures, rather than a clear phase transition, as it was expected. At 450 °C the monoclinic phase predominates, while with higher temperature the cubic phase is more preferred. More specifically, the reflections at $2\theta = 16.6$ °, 17.3 ° and 35.8 ° are changing with annealing temperature and thus, indicate differences in the crystal structure being attributed to a phase change from monoclinic to cubic phase for higher temperatures. The ratio of the phase mixture changes, shown in Figure 2. For a better understanding of the phase stability, we are now studying theoretical phase stability, which can further explain our experimental results.

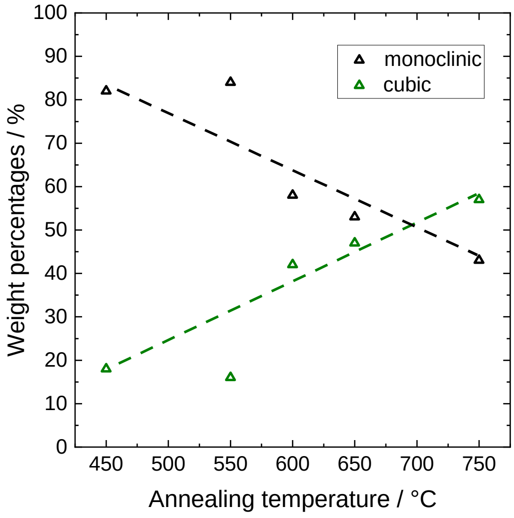

Figure 2: Weight percentages of the monoclinic and cubic phase in the annealed samples Li-Sc-Cl at different temperatures.

2.) Substitution of Zr^{4+} and Mg^{2+} in Li-Sc-Cl to understand the influence of carrier concentration

In studies of halides, for example Zr^{4+} in Li_3ErCl_6, Li_3YCl_6 or Li_3InCl_6, it was shown that the variation of the lithium carrier concentration has a significant influence on the lithium substructure and conductivity. For the spinel structure, there is only one report so far showing the influence of alivoalent substitution of In^{3+} in $Li_2Sc_{2/3}Cl_4$ exists. We studied the aliovalent substitution series of Zr^{4+} and Mg^{2+} in $Li_2Sc_{2/3}Cl_4$ varied the lithium carrier density and therefore should influence the lithium sub lattice and ionic transport. The Li_2MgCl_4 spinel crystallizes in the same space group as $Li_2Sc_{2/3}Cl_4$, whereas the latter has two additional Li^+ positions.

In addition to the above synthesized Li-Sc-Cl samples, the substitution series $Li_{3-x}Sc_{1-x}Zr_xCl_6$ and $Li_{3+x}Sc_{1-x}Mg_xCl_6$ for x = 0.1, 0.2 and 0.3 were mechanochemically synthesized by using the precursors LiCl, $ScCl_3$ and $MgCl_2$ or $ZrCl_4$ in stoichiometric amounts and annealing the precursor mixtures afterwards at 650 °C with subsequent air-quenching.

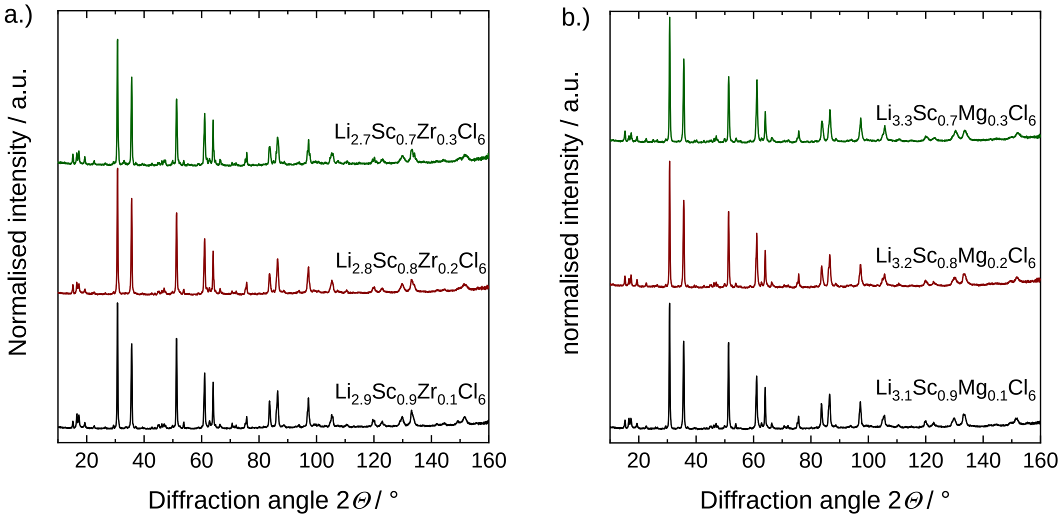

Figure 3: a.) Stacked neutron powder diffraction pattern of the $Li_{3\text{-}x}Sc_{1\text{-}x}Zr_xCl_6$ and b.) $Li_{3+x}Sc_{1\text{-}x}Mg_xCl_6$ substitution series.

First refinements of the neutron diffraction data for the Mg^{2+} substituted sample suggest a preference of cubic phase over the monoclinic phase in compareison to the unsubstituted phase. For a more reliable refinement, the crystal structure at the annealing temperature of 650 °C needs to be fully understood whether it is a phase mixture or pure compound. Within the space group of $Li_2Sc_{2/3}Cl_4$ a honeycomb-like octahedra pattern can be observed which is prone to stacking faults (*Chem. Mater.* **2022**, *34*, 3227−3235, *J. Am. Chem. Soc.* **2022**, *144*, 5795−5811). These complicate the refinement and can be one explanation for the instability of the refinements at the moment.

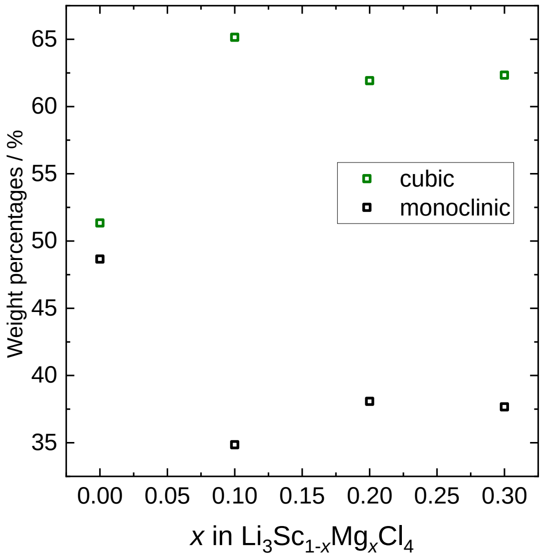

Figure 3: Weight percentages of the cubic and monoclinic phase of the substitution series $Li_{3+x}Sc_{1\text{-}x}Mg_xCl_6$.