Experimental report

29/07/2024

Proposal:	**5-24-730**	**Council:**	10/2023
Title:	Elucidation the role of Zr ordering on Li lattice dynamics of Li2ZrCl6 derivatives electrolytes for all-solid-state batteries		
Research area:	Materials		

This proposal is a new proposal

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Samples:
Li2ZrCl6
Li2.1Zr0.9Fe0.1Cl6
Li3YCl6
Li2+2xZr1-xZnxCl6 (x=0.1, 0.15)
Li2+2xZr1-xMgxCl6 (x=0.1, 0.15)
Li2.5Zr0.75Fe0.25Cl6

Instrument	Requested days	Allocated days	From	To
D2B	3	3	08/12/2023 08/04/2024	10/12/2023 09/04/2024

Abstract:

The development of fast Li conducting solid state electrolytes is essential for the next generation of all-solid-state batteries. Halide electrolytes are a promising family of materials, but the link between their crystal structure and Li kinetics is still not well understood, preventing new routes for further optimisation. We have synthesised a novel family of substituted Li2ZrCl6 halides based on non-critical low-cost elements and proved that conductivity is affected by the type and amount of dopant. Our preliminary simulations suggest that this could be associated with a certain degree of Zr disorder that facilitates a lithium divacancy mechanism in the ab plane, making the conduction pseudo-3D in the material. Temperature-dependent neutron diffraction studies are needed to elucidate key structural factors affecting Li dynamics in the lattice of these new highly conductive solid electrolytes.

Abstract

The development of fast Li conducting solid state electrolytes is essential for the next generation of all-solid-state batteries. Halide electrolytes are a promising family of materials, but the link between their crystal structure and Li kinetics is still not well understood, preventing new routes for further optimisation. We have synthesised a novel family of substituted Li_2ZrCl_6 (LZC) halides based on non-critical low-cost elements and proved that conductivity is affected by the type and amount of dopant. Our preliminary simulations suggest that this could be associated with a certain degree of Zr disorder that facilitates a lithium divacancy mechanism in the ab plane, making the conduction pseudo-3D in the material. Temperature-dependent neutron diffraction studies are needed to elucidate key structural factors affecting Li dynamics in the lattice of these new highly conductive solid electrolytes.

Experimental set-up

In this experiment we have measured the temperature structural evolution of a novel family of solid electrolytes ($Li_{2+2y}Zr_{1-x}M_xCl_6$ where M = Zn, Mg and Fe) with high Li^+ conductivities which have been proposed as promising candidates for Li All Solid-State Batteries (LiASSBs). Neutron powder diffraction (NPD) data were collected in the diffractometer D2B. The high intensity mode ($\Delta d/d \geq 2x10^{-3}$) was selected, with a neutron wavelength $\lambda = 1.594$ Å within the angular 2Θ range from 5° to 165°and the selected temperature range was from -53 to 400ºC by using both a cryo-furnace (-53 – 100ºC) and a HT-furnace (200 – 400ºC) in order to study the temperature dependence of Li dynamics on these compounds.

About 3 g of each sample were loaded into a vanadium cylinder with an Indium wire as sealing. The loading of the samples was done in an Ar filled Glovebox with a moisture and oxygen levels below 0.5 ppm.

A total of five samples have been measured

The collection time was about 3h per pattern.

Preliminary Results

The obtained RT-NPD for the starting composition sample (Li_2ZrCl_6) is shown in ***Fig.*** . The sample has shown to crystallize on the trigonal *P*-3*m*1 space group as has been previously reported, however, we found a need of introducing a certain degree of disorder on the Zr sites in order to get a good fit. The refined cells parameters are as follows *a*=*b*= 10.968728Å and *c* = 5.931590Å.

Also, we have been able to prove previous simulations that has been done in our group, that suggested a 3D Li^+ diffusion allowed by the above mentioned Zr disorder.

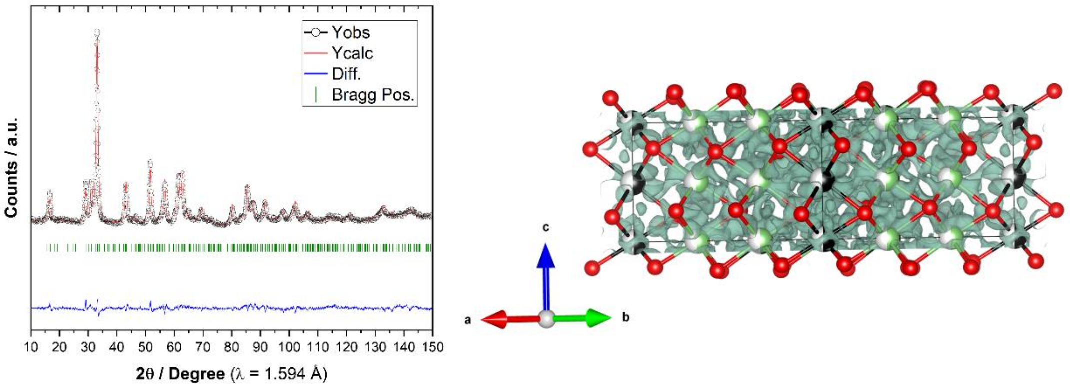

Fig. 1. (left)Rietveld refinement of the Li_2ZrCl_6 at RT on the *P*-3*m*1 space group. (right) BVEL extracted from NPD data. Zirconium, chlorine and lithium atoms are shown in black, red and light green respectively.

The refined atomic positions and occupancies can be found in the table below:

Atom	x	y	z	Occ.
Cl1	0.10733	-0.10733	0.74544	0.500
Cl2	0.22686	-0.22686	0.25048	0.500
Cl3	0.44053	-0.22686	0.74070	0.500
Zr1	0.00000	0.00000	0.00000	0.044
Zr2	0.33333	0.66667	0.50000	0.094
Zr3	0.33333	0.66667	0.50000	0.075
Zr4	0.00000	0.00000	0.50000	0.042
Li1	0.33333	0.00000	0.00000	0.250
Li2	0.33333	0.00000	0.50000	0.250

In order to study the effect of the aliovalent substitution of the Zr by other non-critical metals, we've studied three different aliovalent substitutions which are Fe^{3+}, Mg^{2+} and Zn^{2+}-substituted LZC.

Here, we show the NPD pattern of the Mg-substituted $Li_{2.3}Zr_{0.85}Mg_{0.15}Cl_6$ (LZ85M15C) at RT. (Fig. 2) It can be noticed in that case, that two phases are required to fit the experimental data. This secondary phase has been found to be a small LiCl segregation.

Also, the cell parameters have shown a subtle expansion and the fitted values are now *a*=*b*= 10.97970 Å and *c* = 5.95406 Å. This slight change may be attributed to some electrostatic repulsion phenomena, as the ionic radii for Zr(IV) and Mg(II) in octahedral coordination is the same (0.72 Å)

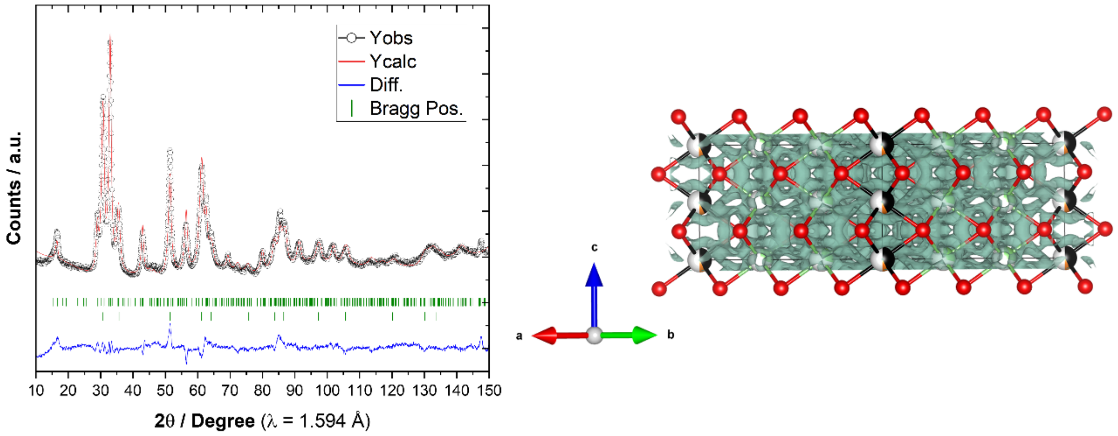

Fig. 2. (left)Rietveld refinement of the $Li_{2.3}Zr_{0.85}Mg_{0.15}Cl_6$ at RT on the *P*-3*m*1 space group. (right) BVEL extracted from NPD data. Zirconium, magnesium, chlorine and lithium atoms are shown in black, orange, red and light green respectively.

The refined atomic positions and occupancies for the Mg^{2+}-substituted sample are summarized below:

Atom	x	y	z	Occ.
Cl1	0.10733	-0.10733	0.74544	0.500
Cl2	0.22686	-0.22686	0.25048	0.500
Cl3	0.44053	-0.22686	0.74070	0.500
Zr1	0.00000	0.00000	0.00000	0.035
Mg1	0.00000	0.00000	0.00000	0.006
Zr2	0.33333	0.66667	0.50000	0.071
Mg2	0.33333	0.66667	0.50000	0.013
Zr3	0.33333	0.66667	0.50000	0.071
Mg3	0.33333	0.66667	0.50000	0.013
Zr4	0.00000	0.00000	0.50000	0.035
Mg4	0.00000	0.00000	0.50000	0.006
Li1	0.33333	0.00000	0.00000	0.250
Li2	0.33333	0.00000	0.50000	0.250

It is worth mentioning, that Mg seems to be introduced in the Zr sites. Even though, further data analysis is ongoing to study possible site mixing on the Li sites, as the ionic radii for the Li in octahedral coordination (0.76 Å) is not so different compared to the Zr and Mg one (0.72 Å).

It is also visible on the BVEL of the LZ85M15C sample that the Li^+ seems to have a higher mobility compared to the pure LZC structure. This may be related with the expansion of the cell lattice.

However, there is still further data analysis going on, regarding the temperature dependence of the Li mobility on these halide solid electrolytes (HSEs) which will lead to a better understanding of the transport properties and mechanisms of this family of promising solid electrolytes for lithium all solid-state batteries (LiASSBs)