Experimental report

26/12/2025

Proposal: 5-22-842 **Council:** 10/2024

Title: Increasing the ionic conductivity by Fe3+ doping in Li3InCl6 inorganic solid electrolyte

Research area: Materials

This proposal is a new proposal

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Samples: Li3InCl6
Li2ZrCl6
Li3Fe0.1In0.9Cl6
Li3Fe0.2In0.8Cl6
Li3Fe0.4In0.6Cl6
Li3Fe0.3In0.7Cl6
Li2.25Zr0.93Cl6
Li2.5Zr0.87Cl6
Li2.75Zr0.83Cl6
Li3Zr0.75Cl6

Instrument	Requested days	Allocated days	From	To
D20	1	2	04/07/2025	06/07/2025
D1B	1	0		
D2B	2	0		

Abstract:

Cation substitution is considered a suitable strategy to increase the conductivity of
inorganic halides by introducing local disorder (i.e. vacancy generation, site occupation¿). Nonetheless, more studies are needed to clarify the Li-ion diffusion pathways in the crystalline structure that will optimise the dopants' design . With this in mind, we decided to take a well-known inorganic halide, Li3InCl6 (monoclinic, C2/m) and partially substitute the metal ions with Fe3+, for which an increase in conductivity has been observed. In this context, neutrons are needed to characterize the Li-ions within the crystalline structure, which will complement the studies carried out using synchrotron radiation, to study the Li-ion diffusion pathways. Obtained knowledge can be used as a guide for designing novel inorganic halide electrolytes with better electrochemical performance.

Introduction

The presence of point defects and local structural disorder plays a pivotal role in significantly boosting ionic conductivity in solid electrolytes. A widely adopted strategy to enhance this conductivity involves the substitution of cations alongside the incorporation of lithium ions into the material´s lattice structure. In this study, we commenced with the inorganic halide Li_3InCl_6, which crystallizes in a monoclinic structure (monoclinic *C*2/*m*, ICSD No. 04-009-9027) in the form of a layered structure. Gradually, we introduced Li+ ions by decreasing the amount of metal ions (initially In^{3+}, but we also expanded to the Zr-based system). This unique crystalline arrangement forms lithium and metal layers, effectively channeling ionic conduction through well-defined two-dimensional diffusion pathways. Furthermore, the introduction of vacancies within the metal layers by their substitution with Li+ ions facilitates the emergence of additional diffusion routes.

Results of the experiment

Neutron diffraction data for the samples were collected on the D20 diffractometer, sealing the samples inside a glovebox in vanadium cans to prevent air contact. The neutron wavelength was 1.54 Å, and the diffractograms were collected at room temperature. The obtained neutron data were complementary to synchrotron X-ray powder diffraction data acquired at ALBA synchrotron.

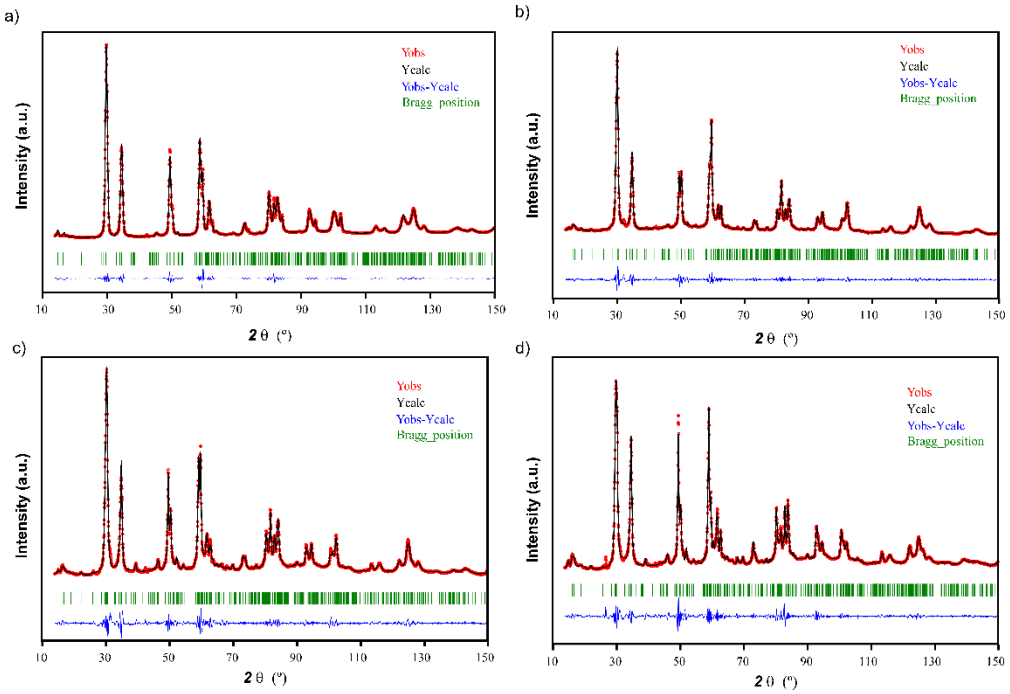

Figure 1. Rietveld refinements over neutron diffraction data of the (a) Li_3InCl_6, b) $Li_{2.75}Zr_{0.81}Cl_6$, c) $Li_{2.25}Zr_{0.93}Cl_6$ and d) Li_2ZrCl_6.

The Rietveld refinement analysis was conducted on neutron diffraction data for each sample. In all cases, the diffraction patterns revealed that the overall crystalline structure remained unchanged at the different measured doping rates. However, slight differences emerged with the incremental addition of Li+ ions. As the concentration of Li+ ions increased and the reduction of metal ions, a significant contraction of the unit cell was observed in the cell parameters (Figure 2). These findings suggest that the incorporation of Li+ ions has a distinct impact on the lattice parameters, highlighting the intricate balance between ion substitution and structural integrity.

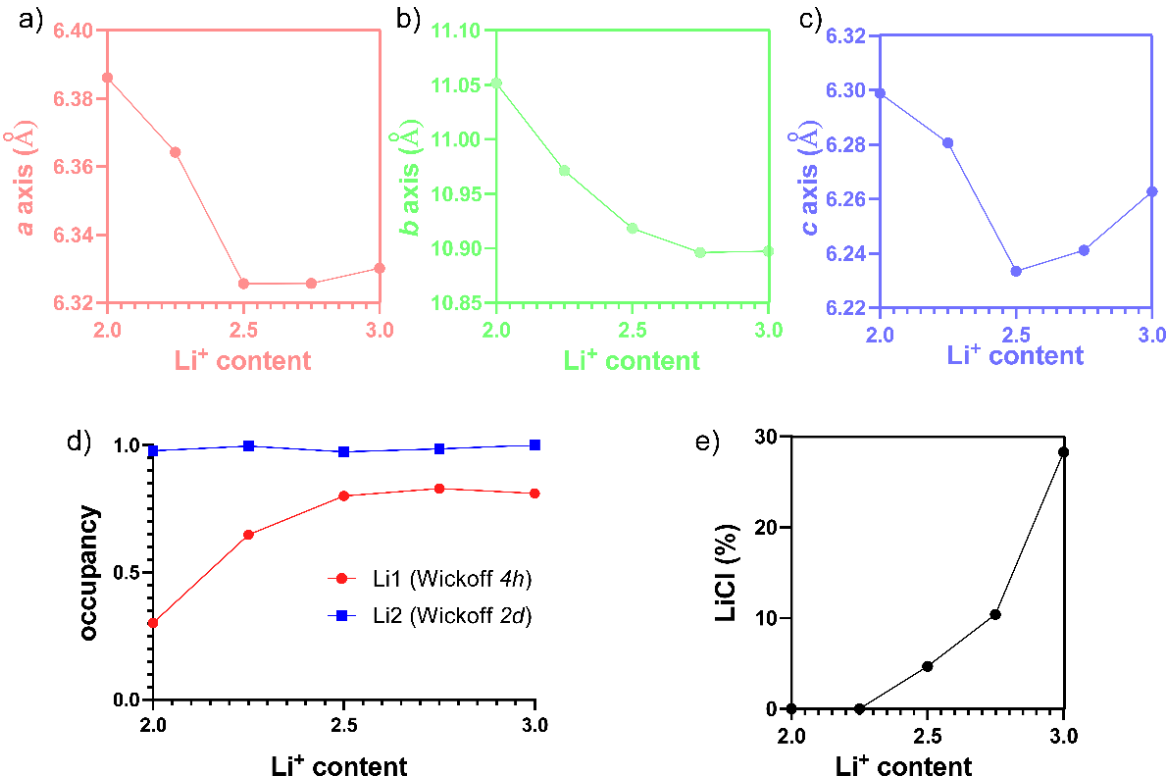

Figure 2. Data extracted from Rietveld refinements for $Li_{2-x}Zr_{1-x}Cl_6$ system: a), b) c) evolution of the cell parameters of the unit cell with respect Li+ content; d) occupancies of lithium atoms at different Li+ content; e) presence of unreacted LiCl.

It was also observed that lithium atoms occupied two distinct positions within the crystal structure: the Wyckoff *2d* and *4h* positions (Figure 3). As the amount of lithium was increased in the system, the occupancy at the *4h* position remained relatively stable, nearing an occupancy value of 1. In contrast, the occupancy at the *2d* position exhibited a gradual increase, ultimately reaching a value of 0.8. This suggests that higher concentrations of Li+ do not effectively integrate into the structure. In contrast, metal sites (Wickoff *4g*) decrease as the lithium content increases, yet no Li+ ions were detected at these sites. Instead of further Li+ incorporation, the diffractogram showed

the presence of unreacted LiCl, indicating that excess lithium was not being accommodated within the lattice framework.

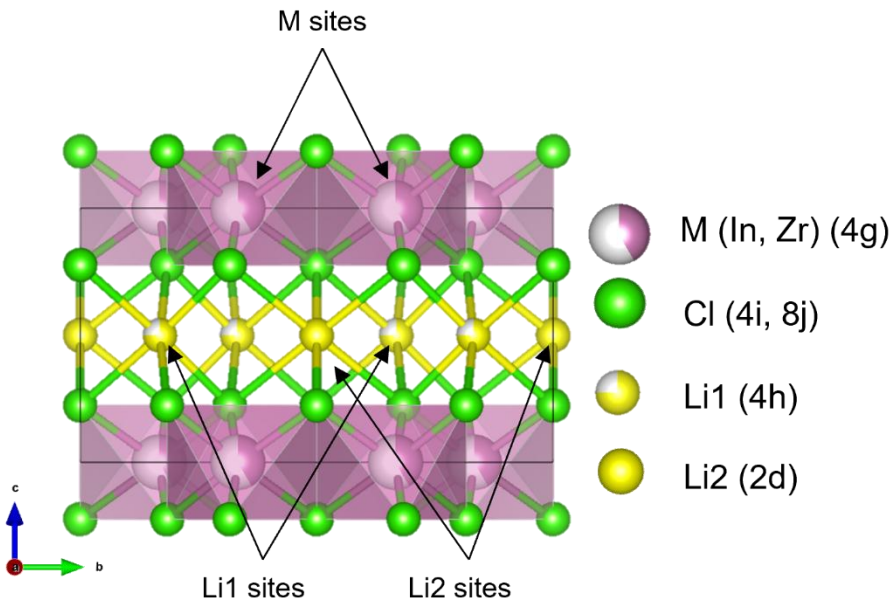

Figure 3. Structural model of $Li_{2+x}M_{1-x}Cl_6$ from the combined refinement of synchrotron and neutron diffraction data.