Experimental report

10/05/2016

Proposal:	**5-22-745**	**Council:**	4/2015
Title:	Experimental visualization of ionic percolation pathways in the fast lithium conductor Li7-3xGaxLa3Zr2O12 and a deuterium-exchanged sample		
Research area:	Materials		

This proposal is a new proposal

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Samples:	Li6.55Ga0.15La3Zr2O12 Li6.55Ga0.15La3Zr2O12 (deuterium-exchanged)

Instrument	Requested days	Allocated days	From	To
D2B	3	3	06/11/2015	09/11/2015

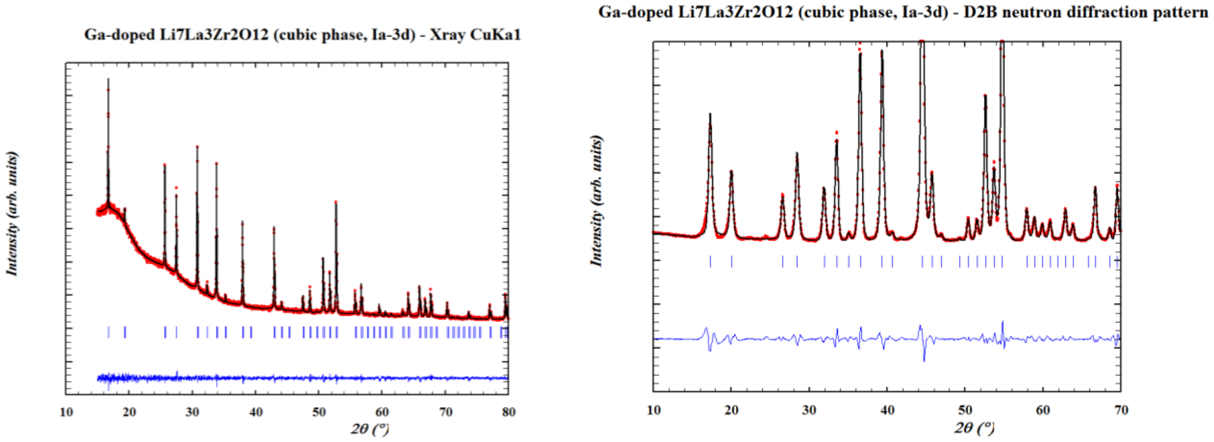
Abstract:

Li-stuffed garnet oxides are promising solid electrolyte materials for lithium batteries. Recently, we reported on a Ga-substituted Li7La3Zr2O12 with lithium ion conductivity reaching 1.3mS/cm at room temperature (the highest obtained for garnet oxides, to date). However, ceramic superionic Li conductors readily suffer from atmospheric corrosion and, in particular Li-H exchange. Much debate has centre on whether the lodged protons progressively block the lithium conduction paths or may exhibit co-mobility in the crystal lattice. Here we seek to clarify this by directly exploring ionic percolation pathways before and after 2D-exchange, as a function of temperature.

The lithium lanthanum zirconate family (LLZO) has aroused an explosion in scientific interest due to its very attractive properties: non-combustibility, wide electrochemical stability window and cubic-phase stability either by aliovalent doping or moisture stabilization. This cubic polymorph is particularly interesting due to predicted cooperative Li-Li motion, with potentially high ionic conductivities (~1 mS/cm). Recently, we demonstrated with a model material ($Li_{6.55}Ga_{0.15}La_3Zr_2O_{12}$) that a strict atmospheric control is necessary to establish high lithium transport. It was found that proton-insertion directly disrupts lithium-lithium interactions leading to slower ion traffic, as shown by NMR relaxometry.[i] Whereas, the proton population can be reversibly altered in solution for unsubstituted LLZO, it is unknown whether the same occurs if aliovalent-substitution was previously in place.[ii]

A neutron diffraction study was thus proposed to correlate lithium and proton positions as a function of temperature for Ga-substituted LLZO. The sample powder prepared was based on the $Li_{6.55}Ga_{0.15}La_3Zr_2O_{12}$ stoichiometry, exhibiting 1.3 mS/cm total ionic conductivity in pellet form. Once synthesized, one portion was protected in a dry Ar atmosphere (<0.1 ppm H_2O), whereas another portion was deuterated in liquid D_2O.

The data analysis has proven challenging however. As shown in Figure 1, all XRD reflections are accounted for by the space group (Ia-3d), but a few minor peaks (2θ=~27°,~56°,~89°) appear in the ND pattern which may indicate a secondary phase impurity or a symmetry change (as proposed by recent works on Ga-doped LLZO synthesized under ambient atmosphere conditions).[iii,iv] Nonetheless, a clear lattice expansion is readily observed for deuterated samples, compared to non-deuterated samples, as plotted in Figure 2.


Ga-doped Li7La3Zr2O12 (cubic phase, Ia-3d) - Xray CuKa1

Ga-doped Li7La3Zr2O12 (cubic phase, Ia-3d) - D2B neutron diffraction pattern

Figure 1 Diffraction patterns of cubic Ga-doped LLZO garnets (unreacted): left = XRD pattern, right = D2B ND pattern.

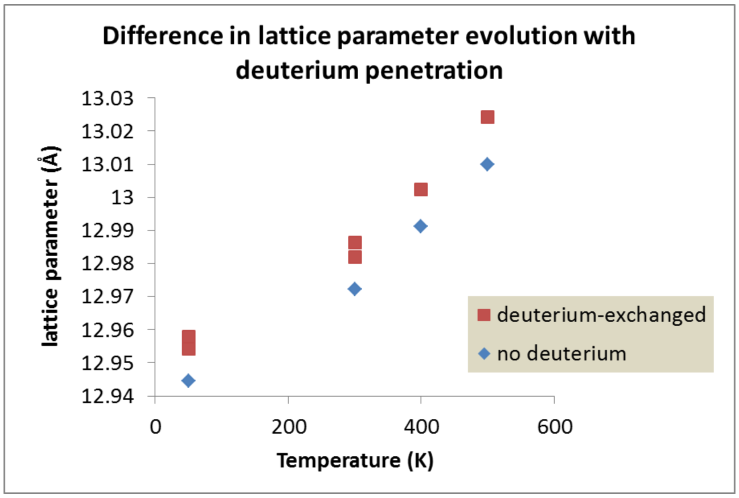


Figure 2 Deuterium penetration effects on the unit cell parameter of $Li_{6.55}Ga_{0.15}La_3Zr_2O_{12}$. Lattice parameters were obtained via LeBail-type fits using the Fullprof Software Suite.

At this point, this preliminary report is limited to confirmed basic results based on global lattice changes. Supporting evidence is currently still being accumulated to support proper elucidation of atomic parameters. A reasonable interpretation will be presented in the final report.

References

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[i] Bernuy Lopez C; Manalastas W; Lopez del Amo JM; Aguadero A; Aguesse F and Kilner JA. Atmosphere Controlled Processing of Ga-Substituted Garnets for High Li-Ion Conductivity Ceramics
Chem Mater. **2015** 26 (12), 3610–3617. doi: 10.1021/cm5008069

[ii] Ma C; Rangasamy E; Liang C; Sakamoto J; More KL and Chi M. Excellent Stability of a Lithium-Ion-Conducting Solid Electrolyte upon Reversible Li+/H+ Exchange in Aqueous Solutions. *Angew. Chem. Int. Ed*.,**2015,** 54: 129–133. doi:10.1002/anie.201408124

[iii] Robben L; Merzlyakova E; Heitjans P; Gesing TM. Symmetry reduction due to gallium substitution in the garnet $Li_{6.43(2)}Ga_{0.52(3)}La_{2.67(4)}Zr_2O_{12}$. Acta Crystallogr E *Crystallogr Commun* **2016**. 72(3): 287–289. doi:10.1107/S2056989016001924.

[iv] Wagner R; Redhammer GJ; Rettenwander D; Senyshyn A: Schmidt W; Wilkening M and Amthauer G. Crystal Structure of Garnet-Related Li-Ion Conductor $Li_{7-3x}Ga_xLa_3Zr_2O_{12}$: Fast Li-Ion Conduction Caused by a Different Cubic Modification? *Chem Mater*. **2016** 28(6):1861-1871. DOI: 10.1021/acs.chemmater.6b00038