Experimental report

23/06/2016

Proposal:	**5-22-735**	**Council:**	10/2014
Title:	Neutron Powder Diffraction Study on Al and Ga in Mixed Doped Li5.8Ga0.4-xAlxLa3Zr2O12 Garnet Solid Solutions with x = 0.00-0.04		
Research area:	Materials		

This proposal is a new proposal

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Samples:
Li5.8Ga0.4Al0.0La3Zr2O12
Li5.8Ga0.3Al0.1La3Zr2O12
Li5.8Ga0.2Al0.2La3Zr2O12
Li5.8Ga0.1Al0.3La3Zr2O12
Li5.8Ga0.0Al0.4La3Zr2O12

Instrument	Requested days	Allocated days	From	To
D20	0	1	06/07/2015	07/07/2015
D2B	0	0		
D1B	1	0		

Abstract:

Cubic Al or Ga doped Li7La3Zr2O12 (LLZO) garnets are the most promising candidates to be used as solid electrolyte in both lithium-ion and Li-oxygen batteries. The location of the dopants in the garnet structure is expected to strongly correlate with the Li-ion transport properties of LLZO. In order to proof this assumption, we systematically varied the site occupation of 24d and 96h sites. This was done by synthesizing mixed-doped Li5.8Ga0.4-xAlxLa3Zr2O12 garnet solid solutions with x = 0.00.4. Indeed, preliminary 7Li MAS NMR measurements show that reducing the 24d site occupation leads to an increase of Li-ion dynamics. For quantification, neutron powder diffraction measurements are needed to get the exact portion of the 24d and 96h occupations. With the obtained data we will finally be able to understand how the 24d or 96h site occupancies influence ionic conductivity.

Several “Beyond Li-Ion Battery” concepts such as all solid-state batteries and hybrid liquid/solid systems envision the use of a solid electrolyte to protect Li-metal anodes. These configurations are very attractive due to the possibility of exceptionally high energy densities and high (dis)charge rates, but they are far from being realized practically due to a number of issues including high interfacial resistance and difficulties associated with fabrication. One of the most promising solid electrolyte systems for these applications is Al or Ga stabilized $Li_7La_3Zr_2O_{12}$ (LLZO) based on high ionic conductivities and apparent stability against reduction by lithium metal. Nevertheless, the fabrication of dense LLZO membranes with high ionic conductivity and low interfacial resistances remains challenging; it definitely requires a better understanding of the structural and electrochemical properties. In this study, the phase transition from garnet (*Ia*-3*d* no.230) to “non-garnet” (*I*-43*d* no.220) space group as a function of composition and the different sintering behavior of Ga and Al stabilized LLZO are identified as important factors in determining the electrochemical properties. The phase transition was located at an Al:Ga substitution ratio of 0.05:0.15 and is accompanied by a significant lowering of the activation energy for Li-ion transport to 0.26 eV. The phase transition combined with microstructural changes concomitant with an increase of the Ga/Al ratio, continuously improves the Li-ion conductivity from 2.6×10^{-4} S cm^{-1} to 1.05×10^{-3} S cm^{-1}, which is close to the calculated maximum for garnet-type materials.

In detail, Polycrystalline samples of $\text{LLZO:Al}_{0:20-x}\text{Ga}_x$.with x = 0.00 – 0.20 were obtained from the pellets and used for the structure determination (XRD, SC-XRD, NPD). Analysis of systematic extinctions of Bragg peaks in the single crystal data sets of the Al-rich compositions unambiguously yield the common garnet–space group *Ia*-3*d* for $\text{LLZO:Al}_{0:20}\text{Ga}_{0.00}$, $\text{LLZO:Al}_{0:15}\text{Ga}_{0.05}$, $\text{LLZO:Al}_{0:10}\text{Ga}_{0.10}$. For compositions LLZO: $\text{Al}_{0.05}\text{Ga}_{0.15}$ and $\text{LLZO:Ga}_{0.20}$, the acentric space group *I*-43*d* was observed as described in detail by Wagner *et al.* (2016), recently.[18] Basic structural data are compiled in Table 1. The Li ion distribution as well as the lattice parameter as a function of the proportion of Ga is illustrated in Fig. 1.

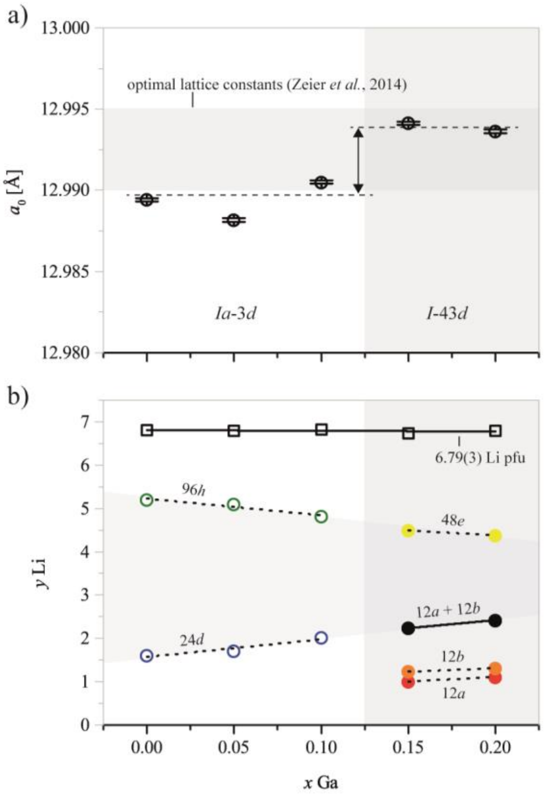

Figure 1. Lattice parameter (a_0) changes(a) and Li site distribution (b) in $Li_{6.4}Al_{0.2-x}Ga_xLa_3Zr_2O_{12}$, with x = 0.00, 0.05, 0.10, 0.15, and 0.20.

Table 1. Basic structural data, and cationic distribution of LLZO:$Al_{0.20-x}Ga_x$ garnets as determined from simultaneous refinement of powder neutron diffraction and single crystal X-ray diffraction data.[a]

x =	0.00	0.05	0.10	0.15	0.20
SG	*Ia*-3*d*	*Ia*-3*d*	*Ia*-3*d*	*I*-43*d*	*I*-43*d*
a_0	12.9894(2)	12.9892(2)	12.9905(2)	12.9941(2)	12.9936(2)
Li_{24d} $\rightarrow_{12a/b}$	1.606(4)	1.706(11)	2.01(2)	1.01(2) 1.23(2)	1.11(3) 1.31(2)
Al_{24d} $\rightarrow_{12a/b}$	0.191(8)	0.198(18)	0.118(14)	0.070(14) -	- -
Ga_{24d} $\rightarrow_{12a/b}$	-	0.048*	0.080*	0.140* -	0.21(2) -
$\square_{24d}$ $\rightarrow_{12a/b}$	1.203	1.048	0.789	0.284 0.268	0.180 0.187
Li_{96h} $\rightarrow_{48e}$	3.750(8)	3.668(11)	4.219(9)	3.03(3)	4.38(2)
$\square_{96h}$ $\rightarrow\square_{48e}$	0.801	0.907	1.190	1.504	1.623
$\mathrm{Li}_{\mathrm{sum}}$	6.805	6.800	6.828	6.734	6.799
$\square_{\mathrm{sum}}$	2.004	1.955	1.974	1.772	1.810
La	2.937(10)	2.947(10)	2.935(10)	2.885(11)	2.951(11)
Zr	2.000*	2.000*	2.000*	2.000*	2.000*

[a] lattice parameter a_0 is given in Å; site occupation values in atoms per formula unit (pfu).*Fixed values, obtained by EDX.

Based on single crystal structure refinements of the samples it is assumed that in SG *Ia*-3*d* Al or Ga is enriched on the tetrahedral 24*d* sites in LLZO; the 16*a* site is fully occupied by Zr^{4+}, and the 24*c* site contains La^{3+} and a small amount of vacancies. With increasing Ga content the amount of vacancies on 24*c* tends to decrease; there is, however, no clear picture from XRD data. In combined refinements, this tendency of decreasing vacancies is tentatively supported. For Ga^{3+} content > 0.1 pfu a change in space group symmetry to *I*-43*d* is observed. For the latter SG there is strong evidence that Ga and Al are enriched onto the tetrahedral 12*a* site, this is observed in both single crystal X-ray diffraction and data from combined refinement (SCXRD and NPD), and supported by DFT calculations. The concentration of vacancies seems to be lower on 12*a* and 12*b* sites in *I*-43*d* SG as compared to *Ia*-3*d*. In addition to the tetrahedral site(s), Li is also found on 96*h* and 48*e* positions, respectively. Combined refinements seem to slightly overestimate the amount of Li on these sites. Consequently, the overall content of Li is right above the ideal value of ~ 6.4 pfu for 0.2 pfu trivalent cations substituted. However, considering the lower La content (according to simultaneous refinement of diffraction data), the Li content is in good agreement according charge neutrality. Moreover, an increase of Li occupation at the 24*d* site is observed. The replacement of Al^{3+} by Ga^{3+} slightly increases the lattice parameter a_0, this finding is evident from the single crystal data. The change of symmetry, however, is not well pronounced in the variation of lattice parameters within the compositions (see Figure 1).

The result is published in:

D. Rettenwander, G. J. Redhammer, F. Preishuber-Pflügl, L. Cheng, L. Miara, R. Wagner, A. Welzl, E. Suard, M. M. Doeff, M. Wilkening, J. Fleig, G. Amthauer *Structural and Electrochemical Consequences of Al and Ga Cosubstitution in* $Li_7La_3Zr_2O_{12}$ *Solid Electrolytes: Chem. Mater.*, **2016**, 28(7), 2384-2392.

CSD – Numbers: 430571 (LLZO:$Al_{0.20}Ga_{0.00}$), 430574 (LLZO:$Al_{0.15}Ga_{0.05}$), 430575 (LLZO:$Al_{0.10}Ga_{0.10}$), 430576 (LLZO:$Al_{0.05}Ga_{0.15}$), 430603 (LLZO:$Al_{0.00}Ga_{0.15}$).