

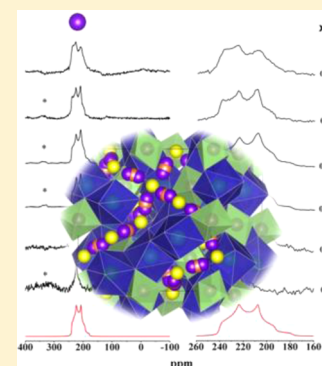
# A Synthesis and Crystal Chemical Study of the Fast Ion Conductor $\text{Li}_{7-3x}\text{Ga}_x\text{La}_3\text{Zr}_2\text{O}_{12}$ with $x = 0.08$ to $0.84$

Daniel Rettenwander,<sup>\*,†</sup> Charles A. Geiger,<sup>†</sup> Martina Tribus,<sup>‡</sup> Peter Tropper,<sup>‡</sup> and Georg Amthauer<sup>†</sup>

<sup>†</sup>Department of Materials Science and Physics, University of Salzburg, Hellbrunnerstrasse 34, A-5020 Salzburg, Austria

<sup>‡</sup>Institute of Mineralogy and Petrography, Faculty of Geo- and Atmospheric Sciences, University of Innsbruck, Innrain 52, A-6020 Innsbruck, Austria

**ABSTRACT:** Fast-conducting phase-pure cubic Ga-bearing  $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$  was obtained using solid-state synthesis methods with 0.08 to 0.52  $\text{Ga}^{3+}$  pfu in the garnet. An upper limit of 0.72  $\text{Ga}^{3+}$  pfu in garnet was obtained, but the synthesis was accompanied by small amounts of  $\text{La}_2\text{Zr}_2\text{O}_{12}$  and  $\text{LiGaO}_3$ . The synthetic products were characterized by X-ray powder diffraction, electron microprobe and SEM analyses, ICP-OES measurements, and  $^{71}\text{Ga}$  MAS NMR spectroscopy. The unit-cell parameter,  $a_0$ , of the various garnets does not vary significantly as a function of  $\text{Ga}^{3+}$  content, with a value of about 12.984(4) Å. Full chemical analyses for the solid solutions were obtained giving:  $\text{Li}_{7.08}\text{Ga}_{0.06}\text{La}_{2.93}\text{Zr}_{2.02}\text{O}_{12}$ ,  $\text{Li}_{6.50}\text{Ga}_{0.15}\text{La}_{2.96}\text{Zr}_{2.05}\text{O}_{12}$ ,  $\text{Li}_{6.48}\text{Ga}_{0.23}\text{La}_{2.93}\text{Zr}_{2.04}\text{O}_{12}$ ,  $\text{Li}_{5.93}\text{Ga}_{0.36}\text{La}_{2.94}\text{Zr}_{2.01}\text{O}_{12}$ ,  $\text{Li}_{5.38}\text{Ga}_{0.53}\text{La}_{2.96}\text{Zr}_{1.99}\text{O}_{12}$ ,  $\text{Li}_{4.82}\text{Ga}_{0.60}\text{La}_{2.96}\text{Zr}_{2.00}\text{O}_{12}$ , and  $\text{Li}_{4.53}\text{Ga}_{0.72}\text{La}_{2.94}\text{Zr}_{1.98}\text{O}_{12}$ . The NMR spectra are interpreted as indicating that  $\text{Ga}^{3+}$  mainly occurs in a distorted 4-fold coordinated environment that probably corresponds to the general  $96h$  crystallographic site of garnet.



## INTRODUCTION

Research has shown that Al-bearing  $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$  (LLZO) with a cubic garnet structure has high ion conductivity (approximately  $10^{-4} \text{ S}\cdot\text{cm}^{-1}$ ).<sup>1</sup> At room temperature, end-member LLZO is tetragonal ( $I4_1/acd$ ) and it has a lower conductivity compared to the “high temperature” cubic modification ( $Ia-3d$ ).<sup>2</sup> The tetragonal phase has a fully ordered arrangement of  $\text{Li}^+$  ions. It has been proposed that by doping LLZO with polyvalent cations the cubic structure is stabilized by introducing vacancies at the Li positions, which act to increase the entropy and reduce the free energy.<sup>3</sup> The stabilization of cubic LLZO through  $\text{Al}^{3+}$  was first reported in 2011<sup>4,5</sup> and confirmed many times thereafter.<sup>6–17</sup> Attention has since been directed also at other dopant cations. Because gallium is located directly below aluminum in the periodic table, it should show similar crystal-chemical behavior as  $\text{Al}^{3+}$  in LLZO. Indeed, the stabilization of cubic LLZO through  $\text{Ga}^{3+}$  has been reported.<sup>17–19</sup>

In spite of the amount of recent study that has been made on the LLZO group of phases, certain aspects are still not understood. Emphasis has been placed on measuring Li-ion conductivity often at the expense of careful compositional and crystal-chemical characterization of the garnet under consideration. The latter are important, if not essential, in order to understand the precise stability and conductivity behavior of LLZO. In terms of Ga-bearing LLZO, there is no information about the amount of  $\text{Ga}^{3+}$  that can be incorporated and its site distribution with the garnet structure.

To obtain a more detailed understanding of the role of super valent cations in LLZO, we synthesized a series of  $\text{Li}_{7-3x}\text{Ga}_x\text{La}_3\text{Zr}_2\text{O}_{12}$  garnets and carefully characterized them chemically and structurally. Characterization was done using X-

ray powder diffraction (XRPD) measurements, electron microprobe analysis (EMPA), inductively coupled plasma optical emission spectroscopy (ICP-OES) measurements, and  $^{71}\text{Ga}$  magic angle spinning (MAS) nuclear magnetic resonance (NMR) spectroscopy.

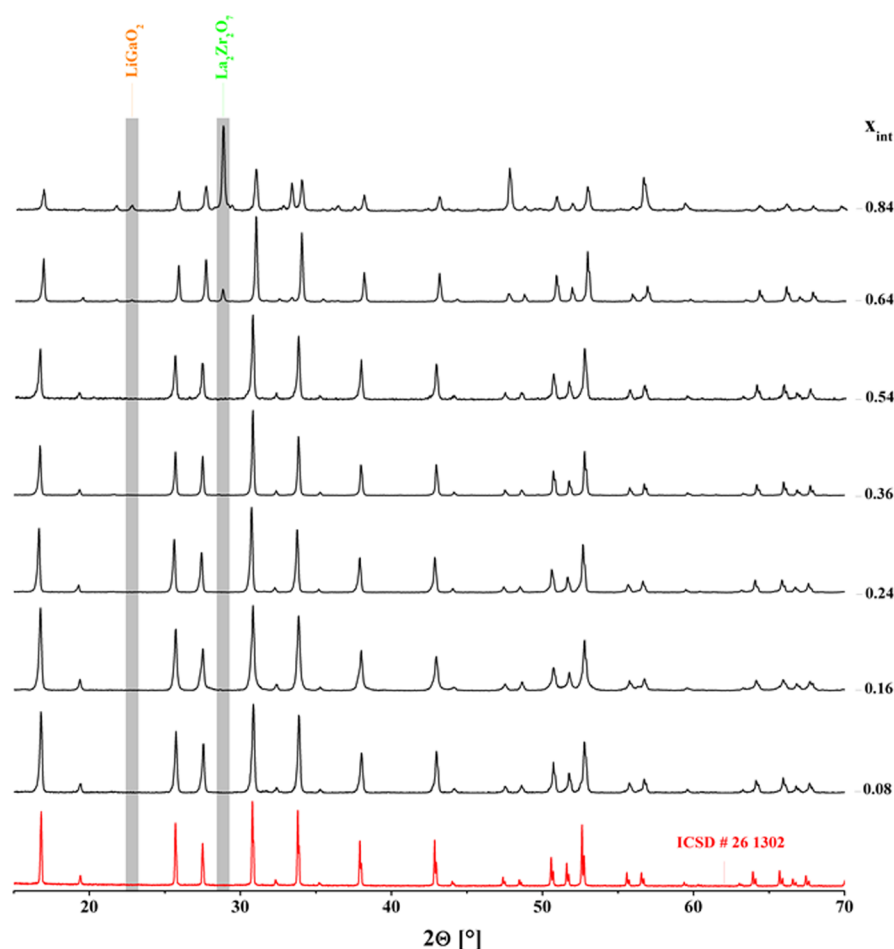
## EXPERIMENTAL SECTION

A series of  $\text{Li}_{7-3x}\text{Ga}_x\text{La}_3\text{Zr}_2\text{O}_{12}$  garnets with intended mole fractions of  $\text{Ga}^{3+}$  ( $x_{\text{int}}$ ) of 0.08–0.84 pfu was synthesized by high-temperature sintering in air. The starting materials were  $\text{Li}_2\text{CO}_3$  (99%, Merck),  $\text{La}_2\text{O}_3$  (99.99%, Aldrich),  $\text{ZrO}_2$  (99.0%, Aldrich), and  $\text{Ga}_2\text{O}_3$  (99.0%, Aldrich). To begin, the starting materials were weighed out in their intended stoichiometric proportions together with an excess of 10 wt %  $\text{Li}_2\text{CO}_3$  to compensate for  $\text{Li}_2\text{O}$  loss during synthesis. After intimate mixing in a ball mill for 8 h, the starting mix was cold-pressed into pellets of 10 mm diameter and 5 mm height. The pellets were placed in a Pt crucible and heated at a rate of 5 °C/min to 900 °C and calcinated for 4 h. The resulting pellets were then removed from the oven, were allowed to cool, and were ground for 15 min and pressed again into pellets. The final sintering step was done at 1050 °C for 17 h in air. A small amount of a given compacted sintered pellet, taken from the middle of the pellet, was ground and used for the XRPD,  $^{71}\text{Ga}$  MAS NMR, and ICP-OES measurements. A polycrystalline chip was used for microprobe analysis.

XRPD measurements were performed with  $\text{Cu K}\alpha$  radiation using a Siemens D8 diffractometer. This was done to characterize the synthetic products in terms of the phases present and to determine the symmetry and unit-cell dimension of the garnet. Data were collected between 10° and 70°  $2\theta$ . The unit-cell lattice parameter,  $a_0$ , and grain size were determined by Rietveld refinement using the program Topas V2.1 (Company Bruker).

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**Figure 1.** XRPD patterns of  $\text{Li}_{7-3x}\text{Ga}_x\text{La}_3\text{Zr}_2\text{O}_{12}$  garnet solid solutions with  $x_{\text{int}} = 0.08\text{--}0.84$ . The diffraction pattern (red) of cubic  $\text{Li}_{7-3x}\text{Al}_x\text{La}_3\text{Zr}_2\text{O}_{12}$  with  $x = 0.24$  is shown for comparison. Only the strongest reflections of non-garnet phases are observed at high  $\text{Ga}^{3+}$  contents and their positions are highlighted with a gray background.

EMPA was done using a JEOL JXA 8100 Superprobe at the Institute of Mineralogy and Petrography at the University of Innsbruck. Small polycrystalline chips, taken from the larger sintered pellets, were embedded in an epoxy holder, and the surface was ground and then polished using diamond paste. Special attention was made with regard to grain sizes, grain boundaries, and textures during analysis. Back-scattered electron (BSE) images were taken to identify small amounts of non-garnet phases. Wavelength-dispersive (WDS) measurements for the elements La, Zr, and Ga were undertaken to characterize the synthetic products in terms of their composition and chemical homogeneity. Analytical measuring conditions were 15 kV accelerating voltage and a 10 nA beam current. The following synthetic standards were used: GaAs (99.99%, Aldrich) for Ga, La-phosphate,  $\text{LaP}_5\text{O}_{14}$ , for La, and zircon,  $\text{ZrSiO}_4$ , for Zr. Measuring times were 20 s at the peak maximum and 10 s for the lower and upper peak background. Twenty point measurements, made on five different garnet grains, were performed to obtain representative compositions for each garnet composition.

ICP-OES measurements, using a Horiba Jobin Yvon Ultima 2 device, were made to determine the Li contents at the University of Ulm, Germany. About 50 mg of garnet, taken from a sintered pellet, were divided into two batches in order to be able to determine the analytical reproducibility. The samples were prepared by placing 15 mg of garnet in 2 mL of aqua regia ( $\text{HCl} + \text{HNO}_3$ ), followed by heating to ensure dissolution of the garnet. Deionized water was then added to obtain 20 mL of solution. One mL aliquots were used for the ICP-OES measurements.

$^{71}\text{Ga}$  MAS NMR spectra were recorded at room temperature on the same  $\text{Ga}^{3+}$ -bearing samples that were characterized by XRPD, EMPA,

and ICP-OES measurements using a Bruker ASX 400 spectrometer at Ruhr University in Bochum, Germany. MAS NMR spectra were collected at 122 MHz (9.4 T) with a spinning rate of 12.5 kHz using a 4 mm MAS probe. Spectra were recorded with a single pulse sequence; the pulse length was 0.6  $\mu\text{s}$ . The spectral width was 125 kHz corresponding to a radio frequency tip angle of about  $15 \pm 5^\circ$ . The signal-to-noise ratio was optimized by a pulse delay of 0.4 s using full relaxation for short pulses. Line broadening of 100 Hz was applied and the first 4–8 points of 1 k measured free induction decay (FID) points were removed because of the strong distortion and low signal. The count of the spectral points was 8 k. Typically, about  $10^6$  scans were acquired for samples with  $x_{\text{int}} < 0.36$  and about  $2 \times 10^5$  for samples with  $x_{\text{int}} \geq 0.24$ . Line shapes were simulated using the STARS simulation package (Varian), with manual adjustment of parameters to match the quadrupolar line shapes typical of the spectra for the samples with  $x_{\text{int}} = 0.24$  to  $x_{\text{int}} = 0.64$ . The  $^{71}\text{Ga}$  chemical shifts are reported relative to aqueous 1 M  $\text{Ga}(\text{NO}_3)_3$ .

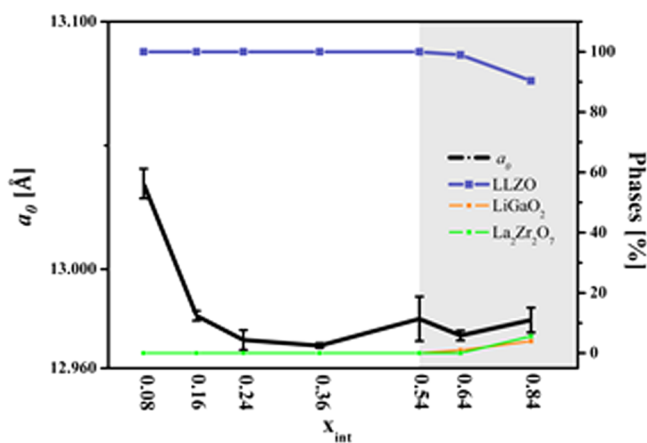
## RESULTS

**Garnet Composition and Lattice Constant.** The XRPD patterns of the various  $\text{Li}_{7-3x}\text{Ga}_x\text{La}_3\text{Zr}_2\text{O}_{12}$  garnets with  $x_{\text{int}} = 0.08, 0.16, 0.24, 0.36, 0.54, 0.64,$  and  $0.84$  are shown in Figure 1, together with the pattern of  $\text{Li}_{7-3x}\text{Al}_x\text{La}_3\text{Zr}_2\text{O}_{12}$  with  $x = 0.24$  (ICSD no. 261302). All garnet compositions exhibit reflections indicating cubic symmetry. There are no indications of reflection splitting indicating a tetragonal garnet phase. All diffraction patterns of garnet with  $x_{\text{int}}$  from 0.08 to 0.54 do not show the presence of any other phase. In the diffraction pattern

of the sample with  $x_{\text{int}} = 0.64$ , just one weak reflection is observed and it can be assigned to  $\text{La}_2\text{Zr}_2\text{O}_7$  occurring at roughly the 1% level. For the garnet with  $x_{\text{int}} = 0.84$ , about 4%  $\text{LiGaO}_2$  and 6%  $\text{La}_2\text{Zr}_2\text{O}_7$  are calculated from Rietveld analysis. The unit-cell constant,  $a_0$ , and a determination of the amounts of the different phases were evaluated by Rietveld analysis. The results are summarized in Table 1 and shown in Figure 2. The

**Table 1.** Unit-Cell Parameter of  $\text{Li}_{7-3x}\text{Ga}_x\text{La}_3\text{Zr}_2\text{O}_{12}$  with  $x_{\text{int}} = 0.08\text{--}0.84$  and the Amount of Phases in the Different Syntheses Obtained by Rietveld Refinement

$x_{\text{int}}$	$a_0$ [Å]	LLZO [%]	$\text{La}_2\text{Zr}_2\text{O}_7$ [%]	$\text{LiGaO}_2$ [%]
0.08	13.034(6)	100	0	0
0.16	12.981(2)	100	0	0
0.24	12.971(4)	100	0	0
0.36	12.969(1)	100	0	0
0.54	12.979(9)	100	0	0
0.64	12.973(2)	>99	<1	0
0.84	12.979(5)	90	6	4



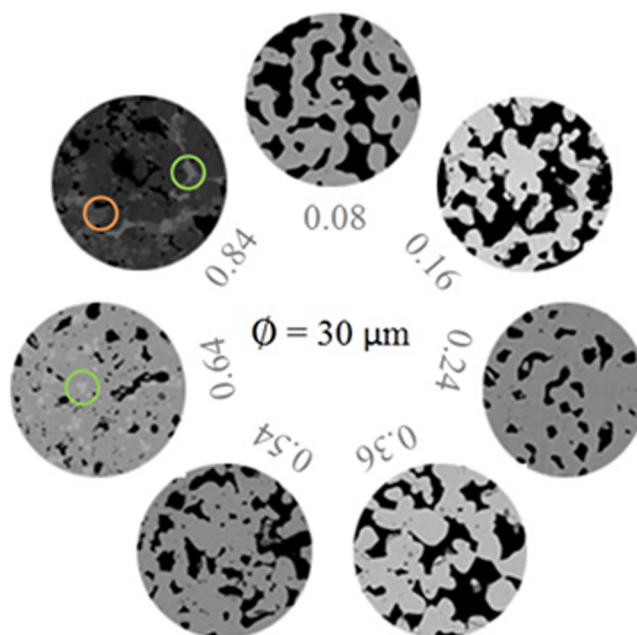
**Figure 2.** Lattice parameter,  $a_0$ , and amount of phases obtained in the synthesis experiments as a function of the intended  $\text{Ga}^{3+}$  concentration in LLZO.

unit-cell constant of garnet with  $x_{\text{int}} = 0.08$  is 13.034(6) Å, and this value decreases slightly to 12.971(4) Å for garnet with  $x_{\text{int}} = 0.24$ . More Ga-rich garnets have a similar  $a_0$  value of 12.979(5) for the sample with  $x_{\text{int}} = 0.84$ . The  $a_0$  values are similar to Al-bearing LLZO with  $a_0 = 12.975(1)$  Å or to Fe-bearing LLZO with  $a_0 = 12.986(1)$  Å.<sup>5,20</sup>

The X-ray reflections for Ga-bearing LLZO are broader than those of Al-bearing LLZO and increase, especially at small  $2\theta$ , with increasing  $\text{Ga}^{3+}$  concentration.

**Phase Identification and Compositional Homogeneity (EMPA).** BSE images of polycrystalline chips made with the EPMA are shown in Figure 3. Examination reveals only garnet and no other phases for compositions from  $x_{\text{int}} = 0.08$  up to  $x_{\text{int}} = 0.54$ . Garnet crystal diameters are  $\sim 10$  μm.  $\text{La}_2\text{Zr}_2\text{O}_7$  could be identified in the sample with  $x_{\text{int}} = 0.64$  pfu and  $\text{La}_2\text{Zr}_2\text{O}_7$  and  $\text{LiGaO}_3$  in the sample with  $x_{\text{int}} = 0.84$  pfu. The density of the various samples appears to increase with increasing  $\text{Ga}^{3+}$  content.

**Chemical Composition (EMPA and ICP-OES).** The chemical analyses obtained using EMPA and ICP-OES measurements are reported in Tables 2 and 3 and shown in Figure 4. Ga, La, and Zr were measured by electron microprobe. Because Li cannot be measured by electron



**Figure 3.** BSE images of the various  $\text{Li}_{7-3x}\text{Ga}_x\text{La}_3\text{Zr}_2\text{O}_{12}$  samples with  $x_{\text{int}} = 0.08\text{--}0.84$ . Only garnet crystals are observed from  $x_{\text{int}} = 0.08$  to  $x_{\text{int}} = 0.54$ . The dark regions are holes in the surface of the sample. The orange circle shows the phase  $\text{LiGaO}_3$ , and green circles show  $\text{La}_2\text{Zr}_2\text{O}_7$ . The diameter of each total sample circle is 30 μm.

**Table 2.** EMPA (Ga, La, Zr) and ICP-OES (Li) Results for  $\text{Li}_{7-3x}\text{Ga}_x\text{La}_3\text{Zr}_2\text{O}_{12}$  with  $x_{\text{int}} = 0.08\text{--}0.84$  in wt %

$x_{\text{int}}$	$\text{Ga}_2\text{O}_3$	$\text{Li}_2\text{O}^a$	$\text{La}_2\text{O}_3$	$\text{ZrO}_2$	total
0.08	0.73(4)	11.83	57.16(12)	29.79(35)	99.51(51)
0.16	1.83(8)	10.49	56.49(70)	29.88(35)	98.69(14)
0.24	2.78(8)	10.42	56.57(23)	29.63(35)	99.40(50)
0.36	4.31(10)	9.90	55.86(57)	29.11(35)	99.18(10)
0.54	6.15(4)	9.06	55.91(19)	28.59(35)	99.71(33)
0.64	6.92(11)	8.37 <sup>b</sup>	54.98(78)	28.65(17)	100.00
0.84	8.33(9)	7.80 <sup>b</sup>	54.65(73)	28.29(17)	100.00

<sup>a</sup>Measured by ICP-OES. Data were normalized to 100 wt % for the elemental oxides. Values in brackets are the standard deviation based on 20 point analyses. <sup>b</sup>Values were calculated according to  $[\text{Li}_2\text{O}] = 100 - [\text{Ga}_2\text{O}_3] - [\text{La}_2\text{O}_3] - [\text{ZrO}_2]$ .

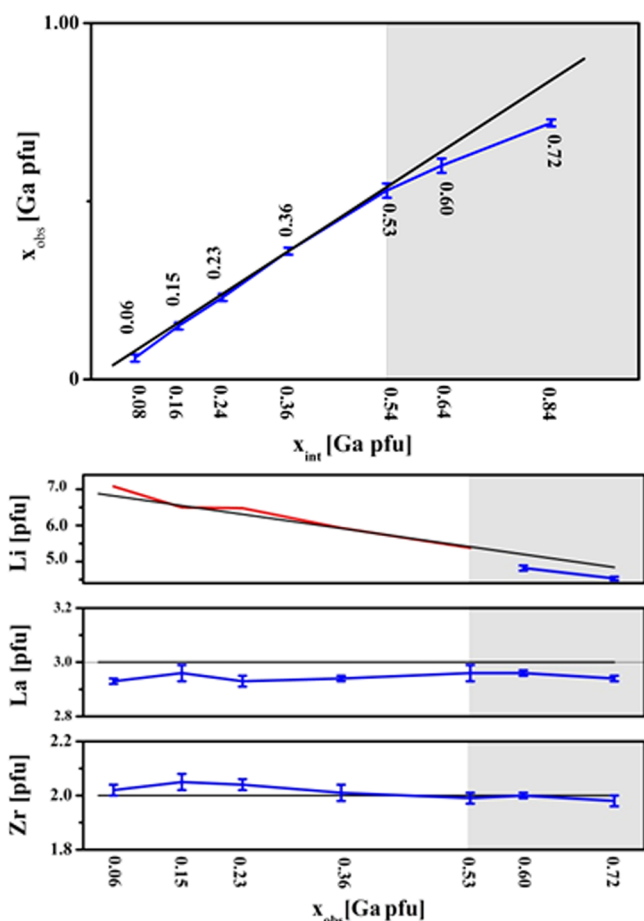
**Table 3.** Crystal Chemical Formulae of the  $\text{Li}_{7-3x}\text{Ga}_x\text{La}_3\text{Zr}_2\text{O}_{12}$  Samples<sup>a</sup>

$x_{\text{int}}$	$\text{Ga}^{3+}$	$\text{Li}^+$	$\text{La}^{3+}$	$\text{Zr}^{4+}$
0.08	0.06(1)	7.08	2.93(1)	2.02(2)
0.16	0.15(1)	6.50	2.96(3)	2.05(3)
0.24	0.23(1)	6.48	2.93(2)	2.04(2)
0.36	0.36(1)	5.93	2.94(1)	2.01(3)
0.54	0.53(2)	5.38	2.96(3)	1.99(2)
0.64	0.60(2)	4.82	2.96(1)	2.00(1)
0.84	0.72(1)	4.53	2.94(1)	1.98(2)

<sup>a</sup>Calculated using the values given in Table 2 on the basis of 12 oxygen atoms per formula unit [pfu].

microprobe analysis, the  $\text{Li}_2\text{O}$  content of those syntheses that yielded only garnet was measured by ICP-OES.

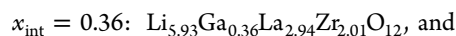
**Crystal Chemical Formula.** The measured  $\text{Ga}^{3+}$  concentrations of the various single phase garnet samples ( $x_{\text{obs}}$ ) are close to the nominal values of the starting material:  $x_{\text{int}} = 0.08 \rightarrow x_{\text{obs}} = 0.06(1)$ ,  $x_{\text{int}} = 0.16 \rightarrow x_{\text{obs}} = 0.15(1)$ ,  $x_{\text{int}} = 0.24 \rightarrow x_{\text{obs}}$



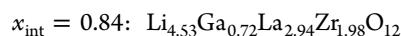
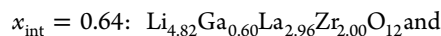
**Figure 4.** Plot of measured vs intended compositions for  $\text{Li}_{7-3x}\text{Ga}_x\text{La}_3\text{Zr}_2\text{O}_{12}$  with  $x_{\text{int}} = 0.08\text{--}0.84$ . The black lines correspond to intended garnet compositions, the blue lines to the EMPA measured values, and the red line to the ICP-OES measurements. The gray area corresponds to those bulk compositions where non-garnet phases are present in the synthetic product.

$= 0.23(1)$ ,  $x_{\text{int}} = 0.36 \rightarrow x_{\text{obs}} = 0.36(1)$ , and  $x_{\text{int}} = 0.54 \rightarrow x_{\text{obs}} = 0.53(2)$ . When additional non-garnet phases are present, the  $\text{Ga}^{3+}$  content in LLZO is lower than that in the starting material:  $x_{\text{int}} = 0.64 \rightarrow x_{\text{obs}} = 0.60(2)$  and  $x_{\text{int}} = 0.84 \rightarrow x_{\text{obs}} = 0.72(1)$ . The Li content measured with ICP-OES ( $\text{Li}_{\text{obs}}$ ) agrees satisfactorily with the Li content ( $\text{Li}_{\text{theo}}$ ) of the starting material:  $x_{\text{int}} = 0.08$ ,  $\text{Li}_{\text{theo}} = 6.82 \rightarrow \text{Li}_{\text{obs}} = 7.08$ ;  $x_{\text{int}} = 0.16$ ,  $\text{Li}_{\text{theo}} = 6.55 \rightarrow \text{Li}_{\text{obs}} = 6.50$ ;  $x_{\text{int}} = 0.24$ ,  $\text{Li}_{\text{theo}} = 6.31 \rightarrow \text{Li}_{\text{obs}} = 6.48$ ;  $x_{\text{int}} = 0.36$ ,  $\text{Li}_{\text{theo}} = 5.92 \rightarrow \text{Li}_{\text{obs}} = 5.93$ ; and  $x_{\text{int}} = 0.54$ ,  $\text{Li}_{\text{theo}} = 5.41 \rightarrow \text{Li}_{\text{obs}} = 5.38$ . For more Ga-rich samples having additional non-garnet phases, the Li content was calculated based on  $[\text{Li}_2\text{O}]_x = 100 - [\text{Ga}_2\text{O}_3] - [\text{La}_2\text{O}_3] - [\text{ZrO}_2]$  and gives for  $x_{\text{int}} = 0.64$ ,  $\text{Li}_{\text{theo}} = 5.08 \rightarrow \text{Li}_{\text{obs}} = 4.82(7)$ , and  $x_{\text{int}} = 0.84$ ,  $\text{Li}_{\text{theo}} = 5.41 \rightarrow \text{Li}_{\text{obs}} = 4.53(5)$ .

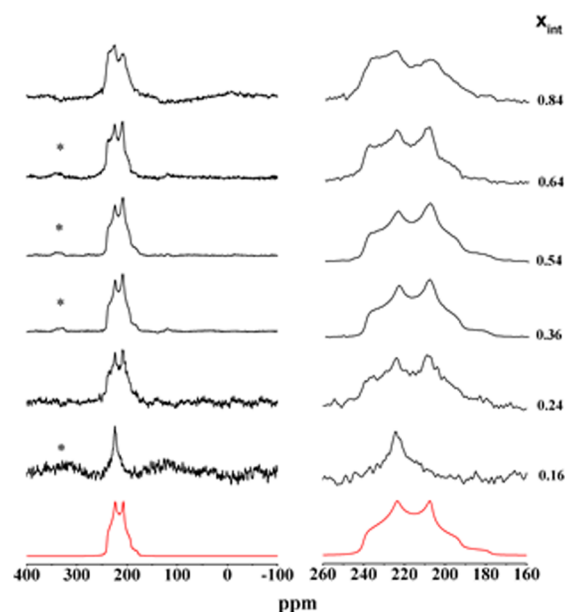
Figure 4 shows that measured La and Zr contents are close to their stoichiometric values of 3.0 and 2.0, respectively, with a maximum deviation of  $\sim 2\%$  pfu (considering the standard deviations). The calculated chemical formulas of the various garnet solid solutions using the EMPA and ICP-OES results are



The chemical formulas of the garnet solid solutions with additional non-garnet phases in the synthetic products are



We note that the  $\text{La}^{3+}$  content in all LLZO samples appears to be slightly too low. This may possibly reflect a systematic analytical artifact related to the La standard used or in the correction procedure. Other reasons could be a possible substitution of  $\text{La}^{3+}$  by  $\text{Li}^+$  or  $\text{Zr}^{4+}$  at the dodecahedral site.



**Figure 5.**  $^{71}\text{Ga}$  MAS NMR spectra of  $\text{Li}_{7-3x}\text{Ga}_x\text{La}_3\text{Zr}_2\text{O}_{12}$  garnets with  $x_{\text{int}} = 0.08\text{--}0.84$ . Asterisks (\*) mark spinning side bands. The spectra on the right are shown over a smaller range of chemical shift values. The spectrum shown in red is simulated for the sample with  $x_{\text{int}} = 0.36$ .

**$^{71}\text{Ga}$  MAS NMR Spectra.** Spectra for the samples with  $x_{\text{int}} = 0.16, 0.24, 0.36, 0.54, 0.64$ , and  $0.84$  are shown in Figure 5.  $^{71}\text{Ga}$  (spin quantum number  $I = 3/2$ , natural abundance 39.6%) is a quadrupole nucleus; the interaction of its rather large quadrupole moment ( $Q = 10.7 \times 10^{-30} \text{ m}^2$ ) with the surrounding electric field gradient results in a central line that is perturbed by second-order effects. Their shape can be simulated well with a single set of NMR parameters, namely an isotropic chemical shift,  $\delta$ , of 244(2) ppm, a quadrupolar coupling constant,  $C_{\text{Q}}$  of 4.0(2) MHz, and an asymmetry parameter,  $\eta_{\text{Q}}$  of 0.46(3). The spectrum of the sample with  $x_{\text{int}} = 0.84$ , which has a slightly different line shape than those in the spectra of the other garnets (Figure 5), also has a NMR resonance with the major component at  $\delta = 244(2)$  ppm. The spectra for samples with  $\text{Ga}^{3+}$  contents,  $x_{\text{int}} \geq 0.36$ , show the best signal to background ratios.

We interpret these spectra, as well as that for  $x_{\text{int}} = 0.24$ , as indicating that  $\text{Ga}^{3+}$  is located at a single structural site in LLZO. The observed  $\delta$  values indicate  $\text{Ga}^{3+}$  with 4-fold

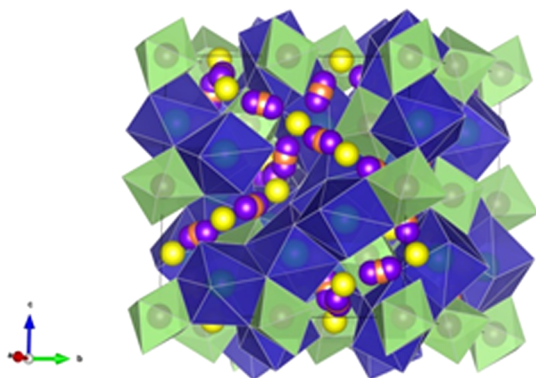
coordination.<sup>21</sup> The rather large  $\eta_Q$  value indicates that  $\text{Ga}^{3+}$  is located at a structural site with no axial symmetry. This might exclude the special crystallographic tetrahedrally coordinated site  $24d$  in garnet with site symmetry  $-4$  from consideration. It should be noted, however, that the local symmetry around  $\text{Ga}^{3+}$  could be lower than that determined by diffraction measurements. The interpretation of the spectrum of the sample with  $x_{\text{int}} = 0.16$  is difficult because the single resonance could be assigned to a small amount of  $\text{Ga}^{3+}$  located at a site with a smaller  $C_Q$ . The spectrum of the sample with  $x_{\text{int}} = 0.84$  could indicate the presence of two Ga-bearing phases. The major phase is clearly Ga-bearing LLZO and the second possibly minor  $\text{LiGaO}_2$ . The latter was identified by XRPD measurements.  $\text{LiGaO}_2$  has similar NMR parameters of  $\delta = 242(2)$ ,  $C_Q = 3.89(5)$ , and  $\eta_Q = 0.37(2)$  and line shape as Ga-bearing LLZO.<sup>21</sup> This spectrum could represent the superposition of a garnet phase and  $\text{LiGaO}_2$ . A similar situation may be shown in the spectrum with  $x_{\text{int}} = 0.64$ , although no  $\text{LiGaO}_2$  was detected by XRPD or EPMA.

## DISCUSSION

The main goal of this study is to investigate the degree of solid solution and crystal-chemical properties of Ga-bearing LLZO garnet. To understand our discussion, we provide a short description of the crystal structure of cubic LLZO garnet.

$\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$  with cubic symmetry  $Ia-3d$  has  $\text{O}^{2-}$  ions that are located at general crystallographic positions,  $96h$ . They form an oxygen-ion framework with interstices occupied by the  $\text{La}^{3+}$  at the 8-fold coordinated position  $24c$  (point symmetry  $222$ ) and by  $\text{Zr}^{4+}$  at the 6-fold coordinated position  $16a$  (point symmetry  $-3$ ).  $\text{Li}^+$  is partially located at the 4-fold coordinated  $24d$  position (point symmetry  $-4$ ) as well as the 6-fold coordinated  $48g$  positions (point symmetry  $2$ ) and a “4-fold” coordinated  $96h$  position (point symmetry  $1$ ). The latter two sites are empty in the conventional garnet structure.<sup>22</sup> The crystal structure is illustrated in Figure 6.

Allen et al. were the first to study  $\text{Ga}^{3+}$  incorporation in Li-oxide garnet.<sup>23</sup> They investigated the conductivity behavior of a garnet of composition  $\text{Li}_{6.75}\text{La}_{3.00}\text{Zr}_{1.75}\text{Ta}_{0.25}\text{O}_{12.00}$  and two compositions with  $\text{Ga}^{3+}$  or  $\text{Al}^{3+}$  doping. The samples were prepared from a coprecipitated precursor and calcinated by



**Figure 6.** Crystal structure of cubic LLZO. The blue dodecahedrally coordinated sites ( $24c$ ) are occupied by  $\text{La}^{3+}$  and the green octahedrally coordinated sites ( $16a$ ) by  $\text{Zr}^{4+}$ . The yellow spheres correspond to tetrahedrally coordinated sites ( $24d$ ), the orange spheres to octahedrally coordinated sites ( $48g$ ) and the purple to “4-fold” coordinated sites ( $96h$ ). These three latter sites can potentially be occupied by Li.

solid-state sintering. Garnet without  $\text{Ga}^{3+}$  or  $\text{Al}^{3+}$  showed a slightly higher Li-ion conductivity,  $\sigma$ , at room temperature ( $\sigma = 8.7 \times 10^{-4} \text{ S}\cdot\text{cm}^{-1}$ ) than garnet of composition  $\text{Li}_{6.15}\text{La}_{3.00}\text{Zr}_{1.75}\text{Ta}_{0.25}\text{Ga}_{0.20}\text{O}_{12.00}$  ( $\sigma = 4.1 \times 10^{-4} \text{ S}\cdot\text{cm}^{-1}$ ) and  $\text{Li}_{6.15}\text{La}_{3.00}\text{Zr}_{1.75}\text{Ta}_{0.25}\text{Al}_{0.20}\text{O}_{12.00}$  ( $\sigma = 3.7 \times 10^{-4} \text{ S}\cdot\text{cm}^{-1}$ ). They proposed that  $\text{Ga}^{3+}$  mainly occupies the  $96h$  site, whereas  $\text{Al}^{3+}$  is located at  $24d$  based on considering the work of Geller et al., who reported that  $\text{Ga}^{3+}$  preferred 6-fold coordination in garnet ( $16a$ ).<sup>24</sup> Howard et al. synthesized cubic garnet of composition  $\text{Li}_{5.50}\text{Ga}_{0.50}\text{La}_3\text{Zr}_2\text{O}_{12}$  using solid-state sintering methods.<sup>17</sup> A  $^{71}\text{Ga}$  MAS NMR spectrum showed a single resonance with a chemical shift of  $\sim 221$  ppm. They proposed, in contrast to Allen et al., that  $\text{Ga}^{3+}$  occupies the tetrahedrally coordinated special crystallographic  $24d$  site. A third investigation of Ga-bearing LLZO garnet was undertaken by El Shinawi and Janek.<sup>18</sup> Here, a series of  $\text{Li}_{7-x}\text{Ga}_x\text{La}_3\text{Zr}_2\text{O}_{12}$  garnets, synthesized using sol–gel methods, with  $x = 0.1, 0.2, 0.3, 0.4, 0.5$ , and  $1.0$ , were prepared. XRPD analysis indicated the presence of additional non-garnet phases for LLZO compositions with  $x = 0.1, 0.2, 0.5$ , and  $1.0 \text{ Ga}^{3+}$  pfu. They measured only small  $\text{Ga}^{3+}$  contents directly in garnet. Instead, most  $\text{Ga}^{3+}$  was concentrated at grain boundaries. The non-garnet phases were: (i)  $\text{La}_2\text{Zr}_2\text{O}_7$ , which was present in compositions with  $x = 0.1, 0.2, 0.5$ , and  $1.0 \text{ Ga}^{3+}$  pfu, and (ii)  $\text{LiGaO}_2$ , together with another  $\text{La}^{3+}$ - or  $\text{Zr}^{4+}$ -containing phase, for samples with  $x > 0.5 \text{ Ga}^{3+}$  pfu. In terms of the garnet, they observed increasing ion conductivity with increasing  $\text{Ga}^{3+}$  content.

Our work demonstrates that single phase Ga-bearing LLZO can be synthesized with up to  $x = 0.53 \text{ Ga}^{3+}$  pfu. A  $\text{Ga}^{3+}$  content of up to  $x = 0.72 \text{ Ga}^{3+}$  pfu in garnet can be obtained, but herein it is associated with small amounts of additional non-garnet phases. Our results differ from the unspecified minor amount of  $\text{Ga}^{3+}$  incorporated in LLZO as observed by El Shinawi and Janek.<sup>18</sup> We think this reflects the different sample preparation and synthesis route. For example, in the case of the synthesis of Al-bearing LLZO it has been shown that  $\text{LiAlO}_2$  can occur at grain boundaries or that the  $\text{Al}^{3+}$  is incorporated in the garnet, depending upon the exact synthesis conditions.<sup>25</sup>

Previous studies of Ga-bearing Li-oxide garnet have proposed that  $\text{Ga}^{3+}$  can reside at  $24d$ <sup>17</sup> or at  $96h$ <sup>24</sup>. We think that the large  $\eta_Q$  value that is greater than  $0.40$ , together with the relatively large ionic radius of  $\text{Ga}^{3+}$  ( $r^{(6)} = 0.62 \text{ \AA}$ ),<sup>26</sup> argues for local “4-fold” coordination. We think that this occurs at the  $96h$  site (site symmetry:  $1 \Rightarrow \eta_Q \neq 0$ ). Both observations argue against the proposal that  $\text{Ga}^{3+}$  is located at the “standard garnet” tetrahedrally coordinated  $24d$  site (site symmetry:  $-4 \Rightarrow \eta_Q = 0$ ).

To understand the behavior of  $\text{Ga}^{3+}$  better, one can also consider the case of  $\text{Al}^{3+}$  in LLZO garnet. The latter are better understood in terms of their crystal chemistry, and  $^{27}\text{Al}$  NMR spectra and can be used as a guide to interpret our  $^{71}\text{Ga}$  NMR results. It has been proposed that a relationship between  $^{27}\text{Al}$  and  $^{71}\text{Ga}$  in NMR spectra exists for  $\delta$  as is given by<sup>27</sup>

$$\delta(^{27}\text{Al}) = \delta(^{71}\text{Ga}) + 4.50(\pm 4.90)/2.83(\pm 0.10)$$

Taking  $\delta(^{71}\text{Ga}) \approx 246$  ppm for LLZO from our work, we calculate  $88 \pm 5$  ppm for  $\delta(^{27}\text{Al})$ . An  $^{27}\text{Al}$  NMR resonance with this chemical shift value has been measured for Al-bearing LLZO.<sup>4,5,7,8</sup> It was assigned to  $\text{Al}^{3+}$  at the  $96h$  site by DFT calculations.<sup>28</sup> This analysis also argues, albeit indirectly, for the presence of  $\text{Ga}^{3+}$  at  $96h$  in  $\text{Li}_{7-3x}\text{Ga}_x\text{La}_3\text{Zr}_2\text{O}_{12}$  garnets.

## AUTHOR INFORMATION

### Corresponding Author

\*E-mail: daniel.rettewander@sbg.ac.at.

### Author Contributions

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## REFERENCES

- (1) Murugan, R.; Thangadurai, V.; Weppner, W. *Angew. Chem.* **2007**, *119*, 7925–7928.
- (2) Awaka, J.; Kijima, N.; Hayakawa, H.; Akimoto, J. *J. Solid State Chem.* **2009**, *182*, 2046–2052.
- (3) Bernstein, N.; Johannes, M. D.; Hoang, K. *Phys. Rev. Lett.* **2012**, *109*, 205702.
- (4) Buschmann, H.; Dölle, J.; Berendts, S.; Kuhn, A.; Bottke, P.; Wilkening, M.; Heitjans, P.; Senyshyn, A.; Ehrenberg, H.; Lotnyk, A.; Duppel, V.; Kienle, L.; Janek, J. *Phys. Chem. Chem. Phys.* **2011**, *13*, 19378–19392.
- (5) Geiger, C. A.; Alekseev, E.; Lazic, B.; Fisch, M.; Armbruster, T.; Langner, R.; Fechtelkord, M.; Kim, N.; Pettke, T.; Weppner, W. *Inorg. Chem.* **2011**, *50*, 1089–1097.
- (6) Li, Y.; Han, J.-T.; Wang, C.-A.; Vogel, S. C.; Xie, H.; Xu, M.; Goodenough, J. B. *J. Power Sources* **2012**, *209*, 278–281.
- (7) Düvel, A.; Kuhn, A.; Robben, L.; Wilkening, M.; Heitjans, P. *J. Phys. Chem. C* **2012**, *116*, 15192–15202.
- (8) Hubaud, A. A.; Schroeder, D. J.; Key, B.; Ingram, B. J.; Dogan, F.; Vaughey, J. T. *J. Mater. Chem. A* **2013**, *1*, 8813–8018.
- (9) Rangasamy, E.; Wolfenstine, J.; Sakamoto, J. *Solid State Ionics* **2012**, *206*, 28–32.
- (10) Kanamura, K.; Kaeriyama, A.; Honda, A.; Yoshida, T.; Sato, Y. US Patent application number 20110053000, 2011.
- (11) Kotobuki, M.; Kanamura, K.; Sato, Y.; Yoshida, T. *J. Power Sources* **2011**, *196*, 7750–7754.
- (12) Kuhn, A.; Choi, J.-Y.; Robben, L.; Tietz, F.; Wilkening, M.; Heitjans, P. *Z. Phys. Chem.* **2012**, *226*, 525–537.
- (13) Jin, Y.; McGinn, P. J. *Electrochim. Acta* **2013**, *89*, 407–412.
- (14) Jin, Y.; McGinn, P. J. *J. Power Sources* **2011**, *196*, 8683–8687.
- (15) Wolfenstine, J.; Sakamoto, J.; Allen, J. L. *J. Mater. Sci.* **2012**, *47*, 4428–4431.
- (16) Tietz, F.; Wegener, T.; Gerhards, M. T.; Giarola, M.; Mariotto, G. *Solid State Ionics* **2013**, *230*, 77–82.
- (17) Howard, M. A.; Clemens, O.; Kendrick, E.; Knight, K. S.; Apperly, P. A.; Anderson, P. A.; Slater, P. R. *Dalton Trans.* **2012**, *41*, 12048–12053.
- (18) El Shinawi, H.; Janek, J. *J. Power Sources* **2013**, *225*, 13–19.
- (19) Skibsted, J.; Nielsen, N. C.; Bildsoe, H.; Jakobsen, H. J. *J. Magn. Reson.* **1991**, *95*, 88–117.
- (20) Rettewander, D.; Geiger, C. A.; Amthauer, G. *Inorg. Chem.* **2013**, *52*, 8005–8009.
- (21) Ash, J. T.; Grandinetti, P. *J. Magn. Reson. Chem.* **2006**, *44*, 823–831.
- (22) Hellner, E.; Gerlich, R.; Koch, E.; Fischer, W. *Physics Data; Fachinformationszentrum Energie, Physik, Mathematik: Karlsruhe, Germany*, 1979; Vol. 16–1, pp 1–16.

(23) Allen, J. L.; Wolfenstine, J.; Rangasamy, E.; Sakamoto, J. *J. Power Sources* **2012**, *206*, 315–319.

(24) Geller, S. *Z. Kristallogr.* **1967**, *125*, 1–47.

(25) Cheng, L.; Park, J. S.; Hou, H.; Zorba, V.; Chen, G.; Richardson, T.; Cabana, J.; Russo, R.; Doeff, M. *J. Mater. Chem. A* **2014**, *2*, 172–181.

(26) Shannon, R. D.; Prewitt, C. T. *Acta Crystallogr., Sect. B: Struct. Sci.* **1969**, *B25*, 925–946.

(27) Bradley, S. M.; Howe, R. F.; Kydd, R. A. *Magn. Reson. Chem.* **1993**, *31*, 883–886.

(28) Rettewander, D.; Blaha, P.; Laskowski, R.; Schwarz, K.; Bottke, P.; Wilkening, M.; Geiger, C. A.; Amthauer, G. *Chem. Mater.* **2014**, *26*, 2617.

## NOTE ADDED AFTER ASAP PUBLICATION

After this paper was published ASAP May 29, 2014, a correction was made to reference citations in the last paragraph of the Discussion section. The corrected version was reposted June 3, 2014.