A Synthesis and Crystal Chemical Study of the Fast Ion Conductor Li$_{7-3x}$Ga$_x$La$_3$Zr$_{2-3x}$O$_{12}$ with $x = 0.08$ to 0.84

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ABSTRACT: Fast-conducting phase-pure cubic Ga-bearing Li$_7$La$_3$Zr$_{2}$O$_{12}$ was obtained using solid-state synthesis methods with 0.08 to 0.52 Ga$^{3+}$ pfu in the garnet. An upper limit of 0.72 Ga$^{3+}$ pfu in garnet was obtained, but the synthesis was accompanied by small amounts of La$_2$Zr$_2$O$_{12}$ and LiGaO$_2$. The synthetic products were characterized by X-ray powder diffraction, electron microprobe and SEM analyses, ICP-OES measurements, and $^{71}$Ga MAS NMR spectroscopy. The unit-cell parameter, $a_0$, of the various garnets does not vary significantly as a function of Ga$^{3+}$ content, with a value of about 12.984(4) Å. Full chemical analyses for the solid solutions were obtained giving: Li$_7$Ga$_{0.04}$La$_3$Zr$_{2}$O$_{12}$, Li$_7$Ga$_{0.11}$La$_3$Zr$_{2}$O$_{12}$, Li$_7$Ga$_{0.16}$La$_3$Zr$_{2}$O$_{12}$, Li$_7$Ga$_{0.22}$La$_3$Zr$_{2}$O$_{12}$, Li$_7$Ga$_{0.28}$La$_3$Zr$_{2}$O$_{12}$, Li$_7$Ga$_{0.60}$La$_3$Zr$_{2}$O$_{12}$, and Li$_7$Ga$_{1.00}$La$_3$Zr$_{2}$O$_{12}$. The NMR spectra are interpreted as indicating that Ga$^{3+}$ mainly occurs in a distorted 4-fold coordinated environment that probably corresponds to the general 96f crystallographic site of garnet.

INTRODUCTION

Research has shown that Al-bearing Li$_7$La$_3$Zr$_{2}$O$_{12}$ (LLZO) with a cubic garnet structure has high ion conductivity (approximately $10^{-4}$ S·cm$^{-1}$). At room temperature, end-member LLZO is tetragonal ($I_4_1/amd$) and has a lower conductivity compared to the “high temperature” cubic modification ($Ia$-3d). The tetragonal phase has a fully ordered arrangement of Li$^+$ ions. It has been proposed that by doping LLZO withivalent cations the cubic structure is stabilized by introducing vacancies at the Li positions, which act to increase the entropy and reduce the free energy. The stabilization of cubic LLZO through Al$^{3+}$ was first reported in 2011 and confirmed many times thereafter. 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 Al$^{3+}$ in LLZO. Indeed, the stabilization of cubic LLZO through Ga$^{3+}$ has been reported.

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 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 Li$_{7-3x}$Ga$_{3x}$La$_3$Zr$_{2-3x}$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 $^{71}$Ga magic angle spinning (MAS) nuclear magnetic resonance (NMR) spectroscopy.
EMPAs 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, LaP$_5$O$_{14}$, for La, and zircon, 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 (HCl + 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.

$^{71}$Ga MAS NMR spectra were recorded at room temperature on the same 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 μs. The spectral width was 125 kHz corresponding to a radio frequency tip angle of about 15 ± 5°. 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 $10^8$ 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 $^{71}$Ga chemical shifts are reported relative to aqueous 1 M Ga(NO$_3$)$_3$.

**RESULTS**

Garnet Composition and Lattice Constant. The XRPD patterns of the various Li$_{7−x}$Ga$_x$La$_3$Zr$_2$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 cubic Li$_{7−x}$Al$_x$La$_3$Zr$_2$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 La$_2$Zr$_2$O$_7$ occurring at roughly the 1% level. For the garnet with $x_{\text{int}} = 0.84$, about 4% LiGaO$_2$ and 6% La$_2$Zr$_2$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 Li$_{7-x}$Ga$_x$La$_{1-x}$Zr$_2$O$_{12}$ with $x_{\text{int}} = 0.08–0.84$ and the Amount of Phases in the Different Syntheses Obtained by Rietveld Refinement

| $x_{\text{int}}$ | $a_0$ [Å] | LLZO [%] | La$_2$Zr$_2$O$_7$ [%] | 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       | 0                   | <1           |
| 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 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.$^{5,20}$

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 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 $\sim 10 \mu$m. La$_2$Zr$_2$O$_7$ could be identified in the sample with $x_{\text{int}} = 0.64$ pfu and La$_2$Zr$_2$O$_7$ and LiGaO$_2$ in the sample with $x_{\text{int}} = 0.84$ pfu. The density of the various samples appears to increase with increasing 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 microprobe analysis, the Li$_2$O content of those syntheses that yielded only garnet was measured by ICP-OES.

Crystal Chemical Formula. The measured Ga$^{3+}$ concentrations of the various single phase garnet samples ($x_{\text{obs}}$) are close to the nominal values of the starting material: $x_{\text{int}} = 0.08 \rightarrow x_{\text{obs}} = 0.06(1)$, $x_{\text{int}} = 0.16 \rightarrow x_{\text{obs}} = 0.15(1)$, $x_{\text{int}} = 0.24 \rightarrow x_{\text{obs}} = 0.23(1)$.
When additional non-garnet phases are present, the Ga\(^{3+}\) content in LLZO is lower than that in the starting material: 
\[ x_{\text{int}} = 0.64 \rightarrow x_{\text{obs}} = 0.60(2) \quad \text{and} \quad x_{\text{int}} = 0.84 \rightarrow x_{\text{obs}} = 0.72(1) \]

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: 
\[ x_{\text{int}} = 0.08, \quad \text{Li}_{\text{theo}} = 6.82 \rightarrow \text{Li}_{\text{obs}} = 6.55 \]
\[ x_{\text{int}} = 0.16, \quad \text{Li}_{\text{theo}} = 6.31 \rightarrow \text{Li}_{\text{obs}} = 6.48 \]
\[ x_{\text{int}} = 0.24, \quad \text{Li}_{\text{theo}} = 5.92 \rightarrow \text{Li}_{\text{obs}} = 5.93 \]
\[ x_{\text{int}} = 0.36, \quad \text{Li}_{\text{theo}} = 5.41 \rightarrow \text{Li}_{\text{obs}} = 5.38 \]

For more Ga-rich samples having additional non-garnet phases, the Li content was calculated based on 
\[ [\text{Li}_2\text{O}] = 100 - [\text{Ga}_2\text{O}_3] - [\text{La}_2\text{O}_3] - [\text{ZrO}_2] \] 
and gives for 
\[ x_{\text{int}} = 0.64, \quad \text{Li}_{\text{theo}} = 5.08 \rightarrow \text{Li}_{\text{obs}} = 4.82(7), \quad \text{and} \quad x_{\text{int}} = 0.84, \quad \text{Li}_{\text{theo}} = 4.51 \rightarrow \text{Li}_{\text{obs}} = 4.53(5). \]

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:

\[ x_{\text{int}} = 0.08: \quad \text{Li}_7\text{Ga}_{0.06}\text{La}_{2.93}\text{Zr}_{2.02}\text{O}_{12}, \quad \text{and} \]
\[ x_{\text{int}} = 0.16: \quad \text{Li}_6\text{Ga}_{0.15}\text{La}_{2.96}\text{Zr}_{2.03}\text{O}_{12} \]
\[ x_{\text{int}} = 0.24: \quad \text{Li}_6\text{Ga}_{0.23}\text{La}_{2.93}\text{Zr}_{2.03}\text{O}_{12} \]

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

\[ x_{\text{int}} = 0.64: \quad \text{Li}_4\text{Ga}_{0.66}\text{La}_{2.92}\text{Zr}_{1.00}\text{O}_{12} \]
\[ x_{\text{int}} = 0.84: \quad \text{Li}_4\text{Ga}_{0.72}\text{La}_{2.92}\text{Zr}_{1.00}\text{O}_{12} \]

We note that the 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 La\(^{3+}\) by Li\(^{+}\) or Zr\(^{4+}\) at the dodecahedral site.

\(^{71}\text{Ga} \text{MAS NMR Spectra.}\) 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, \(C_Q\), of 4.0(2) MHz, and an asymmetry parameter, \(\eta_Q\), 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 \(\delta = 244(2) \text{ ppm}\). The spectra for samples with 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 Ga\(^{3+}\) is located at a single structural site in LLZO. The observed \(\delta\) values indicate Ga\(^{3+}\) with 4-fold...
coordination.\(^{21}\) The rather large \(\eta_4\) value indicates that Ga\(^{3+}\) is located at a structural site with no axial symmetry. This might exclude the special crystallographic tetrahedrally coordinated site 24\(d\) in garnet with site symmetry \(\bar{4}\) from consideration. It should be noted, however, that the local symmetry around Ga\(^{3+}\) could be lower than that determined by diffraction measurements. The interpretation of the spectrum of the sample with \(x_{\text{tot}} = 0.16\) is difficult because the single resonance could be assigned to a small amount of Ga\(^{3+}\) located at a site with a smaller \(C_{\text{L}}\). The spectrum of the sample with \(x_{\text{tot}} = 0.84\) could indicate the presence of two Ga-bearing phases. The major phase is clearly Ga-bearing LLZO and the second possibly minor LiGaO\(_2\). The latter was identified by XRPD measurements. LiGaO\(_2\) has similar NMR parameters of \(\delta = 242(2), C_3 = 3.89(5)\), and \(\eta_4 = 0.37(2)\) and line shape as Ga-bearing LLZO.\(^{21}\) This spectrum could represent the superposition of a garnet phase and LiGaO\(_2\). A similar situation may be shown in the spectrum with \(x_{\text{tot}} = 0.64\), although no 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.

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

Allen et al. were the first to study Ga\(^{3+}\) incorporation in Li-oxide garnet.\(^{23}\) They investigated the conductivity behavior of a garnet of composition Li\(_{\text{La}}\)\(_{\text{Zr}}\)O\(_{12}\) (site symmetry 16\(a\)) and Li\(_{\text{La}}\)\(_{\text{Zr}}\)O\(_{12}\) with site symmetry 24\(c\) (with \(x_{\text{tot}} = 0.16\) and \(x_{\text{tot}} = 0.84\), respectively). They observed increasing ion conductivity with increasing Ga\(^{3+}\) content.

Our work demonstrates that single phase Ga-bearing LLZO can be synthesized with up to \(x = 0.53\) Ga\(^{3+}\) pfu. A Ga\(^{3+}\) content of up to \(x = 0.72\) 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 unreported minor amount of Ga\(^{3+}\) incorporated in LLZO as observed by El Shinawi and Janek.\(^{18}\) 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 LiAlO\(_2\) can occur at grain boundaries or that the Al\(^{3+}\) is incorporated in the garnet, depending upon the exact synthesis conditions.\(^{25}\)

Previous studies of Ga-bearing Li-oxide garnet have proposed that Ga\(^{3+}\) can reside at 24\(d\) or at 96\(h\). We think that the large \(\eta_4\) value that is greater than 0.40, together with the relatively large ionic radius of Ga\(^{3+}\) (\(r^{\text{Ga}} = 0.62\) \(\text{Å}\)),\(^{26}\) argues for local “4-fold” coordination. We think that this occurs at the 96\(h\) site (site symmetry: 1 \(\Rightarrow\) \(\eta_4 \neq 0\)). Both observations argue against the proposal that Ga\(^{3+}\) is located at the “standard garnet” tetrahedrally coordinated 24\(d\) site (site symmetry: \(-4 \Rightarrow \eta_4 = 0\)).

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

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

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