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Synthesis and Crystal Chemistry of the Fast Li-Ion Conductor $Li_7La_3Zr_2O_{12}$ Doped with Fe

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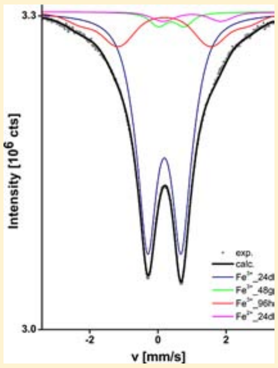
ABSTRACT: Nominal $Li_7La_3Zr_2O_{12}$ (LLZO) garnet, doped with $^{57}Fe_2O_3$, was synthesized by sintering oxides and carbonates at $T = 1100$ °C in air. X-ray powder diffraction measurements show that $Li_{7-3x}Fe^{3+}_xLa_3Zr_2O_{12}$ with $x = 0.19$ crystallizes in the cubic space group $Ia\text{-}3d$, with $a_0 = 12.986(4)$ Å at room temperature. SEM and electron microprobe measurements were made to obtain compositional information and check for the presence of phases other than garnet. Inductively coupled plasma optical emission spectroscopy measurements were made to determine the Li content. ^{57}Fe Mössbauer spectra obtained at 295 and 80 K show that about 96% of the total iron occurs as Fe^{3+} and 4% as Fe^{2+}. Roughly two-thirds of the Fe^{3+} cations are assigned to the tetrahedral site (24*d*) and roughly one-quarter to a highly distorted site (possibly at 96*h*) in the garnet structure. Smaller amounts of Fe^{3+} and Fe^{2+}, around 5% each, occur at other crystallographic sites. On the basis of published ^{27}Al MAS NMR results and analysis of the ^{57}Fe Mössbauer spectra, it appears that at low concentrations Al^{3+} and Fe^{3+} substitute in $Li_7La_3Zr_2O_{12}$ in a similar manner. The aliovalent substitution $Al^{3+}/Fe^{3+} \leftrightarrow 3Li^+$ in LLZO stabilizes the cubic phase and also probably promotes its high Li-ion conductivity.



■ INTRODUCTION

Recent research has shown that a number of Li-containing oxide garnets, the so-called lithium-stuffed garnets having more than three Li cations in the formula unit, are fast-ion conductors.[1] Murugan et al. showed that garnet of nominal composition $Li_7La_3Zr_2O_{12}$ (LLZO) has some of the highest ion conductivities measured to date for any crystalline phase.[2] Unbeknownst to them, their garnet most likely contained small amounts of Al in solid solution, which was incorporated from ceramic crucibles during high-temperature sintering. Geiger et al. showed this and argued further that Al acted to stabilize the cubic LLZO phase, which is a better ion conductor than Al-free tetragonal LLZO.[3] Their proposal was subsequently confirmed by other groups working on Al-doped LLZO.[4−6] Since these findings, much study of a variety of types has been concentrating on LLZO. Because pure nominal $Li_7La_3Zr_2O_{12}$ appears to be tetragonal at room temperature[3] and has lower conductivity than the cubic phase, much work is being directed at doping LLZO with different cations in order to stabilize the cubic structure at room temperatures.

This work reports the first results on the synthesis of LLZO doped with enriched $^{57}Fe_2O_3$. The synthesis procedure is described as well as characterization of the synthetic product using X-ray powder diffraction, SEM, microprobe analysis, and finally ^{57}Fe Mössbauer spectroscopy, the latter being the first such measurements on iron-bearing LLZO.

■ EXPERIMENTAL METHODS

Syntheses were performed by high-temperature sintering methods in air using Li_2CO_3 (99% Merck), La_2O_3 (99.99% Aldrich), ZrO_2 (99.0% Aldrich), and Fe_2O_3 (99.5% Alfa Aesar) in the proportions to obtain garnet of composition $Li_{7-3x}Fe^{3+}_xLa_3Zr_2O_{12}$ with $x = 0.24$. Initial work showed that to obtain good Mössbauer spectra ^{57}Fe-enriched Fe_2O_3 is required. To start, these phases were weighed out with an excess of 10 wt % Li_2CO_3 to compensate for Li_2O loss upon heating. 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. Pellets were placed in a Pt crucible, heated at a rate of 5 °C/min to 900 °C, and calcinated for 4 h. Resulting pellets were then removed from the oven, allowed to cool, and ground for 15 min, pressed again into pellets, and sintered at 1100 °C for 17 h. The oxygen fugacity, f_{O2}, is estimated to be about 0.2 atm from 900 to 1100 °C.

X-ray powder diffraction measurements were performed with a Siemens D500 diffractometer with Cu Kα radiation. Measurements were done to characterize the synthetic product in terms of all phases present and determine the symmetry and unit-cell dimensions of the garnet. Data were collected between 10° and 70° 2θ. The lattice parameter, a_0, was determined using the program Topas V2.1 (Bruker).

Scanning electron microscopy, SEM, analysis was made with a Zeiss Ultra Plus device. Small, dense 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. For analysis, special attention was made with regard to grain sizes, grain boundaries, and textures. EDX measurements were undertaken to characterize the synthetic products in terms of their chemical homogeneity for elements La, Zr, and Fe.

Electron microprobe analysis measurements were done with a JEOL 8100 SUPERPROBE to obtain quantitative chemical analysis (excepting Li) and check for compositional homogeneity. Analytical measuring conditions were a 15 kV accelerating voltage and 10 nA beam current. Standards used were synthetic almandine, $Fe_3Al_2Si_3O_{12}$, for Fe, synthetic La−phosphate, LaP_5O_{14}, for La, and synthetic zircon, $ZrSiO_4$, for Zr. Measuring times were 20 s for the peak maximum and 10 s for the background. The same embedded sample as used for the SEM measurements was analyzed. Because no grain boundaries were

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detectible, 30 point measurements over an area of 200 μm^2 were performed to obtain good compositional characterization.

Inductively coupled plasma optical emission spectroscopy (ICP-OES) measurements were made with a Horiba Jobin Yvon Ultima 2 device at the University of Ulm to determine the Li contents. About 50 mg taken from the sintered pellet was divided into two batches for duplicate measurements in order to be able to test the analytical reproducibility. Samples were prepared by dissolving 15 mg of garnet in 2 mL of aqua regia ($HCl + HNO_3$) followed by heating to complete dissolution of the garnet. Deionized water was then added to obtain 20 mL of solution. Finally, 1 mL aliqouts were taken for ICP-OES measurements.

^{57}Fe Mössbauer spectra were recorded with a multichannel analyzer (1024 channels) operating in conjunction with an electromechanical drive system with symmetric triangular velocity shape. The two simultaneously obtained spectra (512 channels each) were folded and evaluated assuming Lorentzian line shape and quadrupole splitting distributions QSDs with the program Recoil.[7] During the measurements, the source (^{57}Co/Rh 50 mCi) was kept at room temperature whereas the absorber was kept either at room temperature (RT) or liquid nitrogen temperature (LNT) using a bath cryostat. Isomer shift values are reported relative to α-iron at room temperature.

■ RESULTS

The dense pellet obtained after the final synthesis step was beige colored, and a ground sample is shown in Figure 1. The X-ray diffraction pattern of $Li_{7-3x}Fe^{3+}{}_xLa_3Zr_2O_{12}$ with $x = 0.19$ is shown in Figure 2 together with the pattern of "$Li_{7-x}Al_xLa_3Zr_2O_{12}$" with $x = 0.24$ reported by Geiger et al. (ICSD # 261302).[3] Both garnets exhibit reflections indicating cubic symmetry. There are no indications of tetragonal garnet or any other phase in the synthetic product. The unit-cell constant, a_0, was determined as 12.986(4) Å, which is similar to that of Al-bearing LLZO with $a_0 = 12.975(1)$ Å.[3] Reflections associated with Fe-bearing LLZO are broader than those exhibited by Al-bearing LLZO.

Figure 1. Ground powder of $Li_{7-3x}Fe_xLa_3Zr_2O_{12}$ with $x = 0.19$.

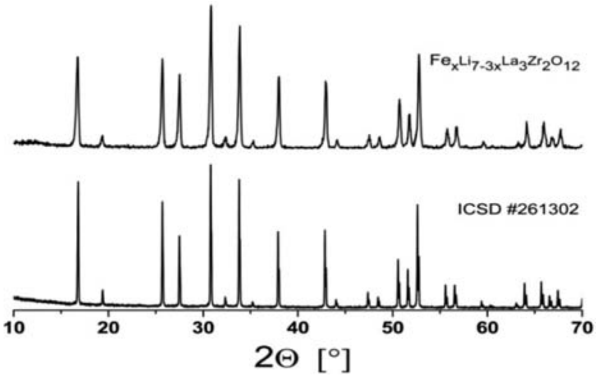

Figure 2. XRPD pattern of $Li_{7-3x}Fe_xLa_3Zr_2O_{12}$ with $x = 0.19$. Diffraction pattern of cubic $Li_{7-3x}Al_xLa_3Zr_2O_{12}$ with $x = 0.24$ is shown for comparison.

SEM examination revealed only garnet and no other phases. A backscattered electron (BSE) photo of a polycrystalline chip is shown in Figure 3. Grain boundaries could not be observed.

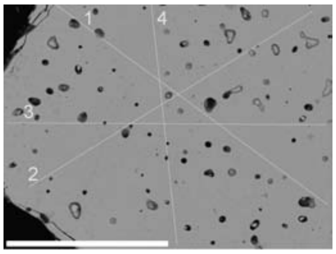

Figure 3. Backscattered electron picture of $Li_{7-3x}Fe_xLa_3Zr_2O_{12}$ with $x = 0.19$. Only garnet crystals are observed. Dark areas are holes in the surface of the sample. Scale line corresponds to 100 μm and the thin white numbered lines to the line scans made to check for compositional homogeneity.

Compositional homogeneity for several garnet crystals was measured by EDX analyses of La, Zr, and Fe. Four line scans with 12 point measurements per scan were made across the polished surface. Standard derivations of the resulting data are 0.30 for La, 0.22 for Zr, and 0.10 for Fe in wt %. Chemical analysis obtained with the electron microprobe is reported in Table 1. Li content, obtained by ICP-OES, is 10.86 wt %. Total oxide sum is 99.95 wt %. Calculation of a crystal-chemical formula was made on the basis of 12 oxygens atoms per formula unit in LLZO and gives $Li_{6.22}Fe_{0.19}La_{3.02}Zr_{2.04}O_{12}$.

Table 1. Microprobe and ICP-OES Results on $Li_{7-3x}Fe_xLa_3Zr_2O_{12}$

	oxides [wt %]	cations [pfu][c]
Fe_2O_3	1.79 (0.03)[a]	0.19
Li_2O	10.86[b]	6.22
La_2O_3	57.76 (0.35)[a]	3.02
ZrO_2	29.54(0.25)[a]	2.04
total	99.95	11.47

[a] Measured by microprobe analysis with standard deviations based on 30 point analyses. [b] Determined by ICP-OES, whereby the total measured oxides are normalized to 100 wt %. [c] Calculated on the basis of 12 oxygen atoms per formula unit [pfu].

^{57}Fe Mössbauer spectra taken at room temperature (RT, 295 K) and liquid nitrogen temperature (LNT, 80 K) are displayed in Figure 4. Model fit parameters are reported in Table 2. It was not possible to evaluate the spectra satisfactorily using quadrupole split doublets with Lorentzian line shapes. Therefore, spectra were fit using quadrupole splitting distributions (QSDs) assuming Voigt line shapes and up to 3 components for each site.[7]

On the basis of the hyperfine isomer-shift and quadrupole-split values, three QSDs are assigned to Fe^{3+} and one weak QSD is assigned to Fe^{2+}. Because the recoil-free fractions of Fe^{3+} and Fe^{2+} at the different crystallographic sites should be most similar at low temperatures, we used the area ratios of the spectrum measured at 80 K for determination of the Fe-site distribution in LLZO.[8] The most intense Fe^{3+} doublet with an area of 68% has an isomer shift of 0.19 mm/s at RT and 0.29 mm/s at 80 K. Its quadrupole splitting, QS, is not temperature

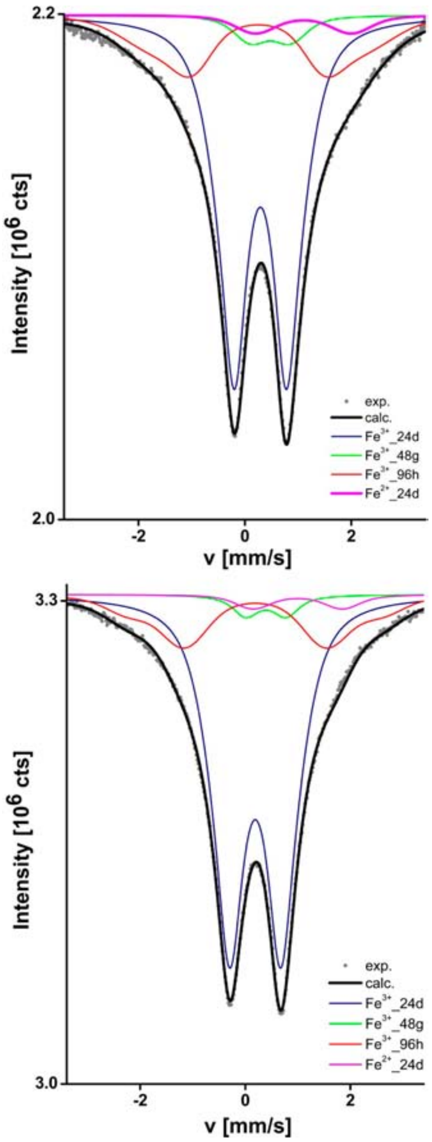

Figure 4. Mössbauer spectra of $Fe_xLi_{7-3x}La_3Zr_2O_{12}$. (Top) Spectrum at 295 K. (Bottom) Spectrum at 80 K. Both spectra were evaluated using 4 quadrupole splitting distributions.

dependent with QS = 1.05 mm/s at RT and QS = 1.07 mm/s at 80 K. On the basis of an analysis of IS values reported for Fe in different coordination states for a large number of phases,[9] this doublet is best assigned to Fe^{3+} in 4-fold coordination. Synthetic silicate garnet of composition $Ca_3(Fe^{3+}_{0.86}Ti^{4+}_{1.14})_2[Si_{1.58}Ti^{4+}_{0.28}Fe^{3+}_{1.14}]_3O_{12}$ gives for Fe^{3+} in tetrahedral coordination IS = 0.20 mm/s and QS = 1.15 mm/s at RT and IS = 0.30 mm/s and QS = 1.15 mm/s at LNT.[10] Therefore, this doublet in the spectra of Fe-bearing LLZO is assigned to Fe^{3+} at the tetrahedral position 24*d*.

The second most intense Fe^{3+} doublet with an area ratio of 22% at 80 K has IS = 0.19 mm/s and QS = 3.20 mm/s at RT and IS = 0.25 mm/s and QS = 3.19 mm/s at 80 K. Isomer shift values indicate tetrahedrally coordinated Fe^{3+}. The unusually large quadrupole splitting indicates a strongly distorted coordination polyhedron. Therefore, this doublet is assigned to Fe^{3+} at the 96*h* position, which is described by some authors as 6-fold coordinated,[11] 5-fold coordinated,[3] or 4-fold coordinated with two longer bonds (>2.6 Å)[12] in different Li–oxide garnets. This 96*h* site is highly distorted, and therefore, the quadrupole splitting for any Fe^{3+} at this site should be large.

A third weak Fe^{3+} doublet with an area of 6% at 80 K has IS = 0.39 mm/s and QS = 0.76 mm/s at RT and IS = 0.48 mm/s and QS = 0.75 mm/s at 80 K. These values are most consistent with Fe^{3+} in octahedral coordination.[9] For the case of synthetic Ti–containing silicate garnet, again, Fe^{3+} at the "normal" octahedral site (16*a*) gives IS = 0.40 mm/s at RT and 0.50 mm/s at 80 K and QS = 0.75 mm/s at RT and QS = 0.75 mm/s at 80 K.[10] Thus, the simplest assignment would place this small amount of Fe^{3+} in LLZO at the 16*a* site normally occupied by Zr. However, because some workers[11] report that Li^+ in LLZO can occupy another 6-fold-coordinated site, namely, 48*g*, it may be that this Fe^{3+} occurs here. We note that based on the microprobe analysis that the 16*a* site should be filled with Zr.

It was not possible to fit the spectra satisfactorily without assuming a small doublet with an intensity of about 4%.

Its isomer shift value is larger than those for the Fe^{3+} doublets, i.e., 1.0 mm/s at RT and 1.1 mm/s at LNT, and thus, it is assigned to Fe^{2+} in tetrahedral coordination. For synthetic Ti-bearing silicate garnet, Fe^{2+} at the tetrahedral 24*d* site gives IS = 1.03 mm/s and QS = 2.09 mm/s at LNT.[10] Because of the low intensity of this doublet, however, a definitive assignment is difficult. Tentatively, we assign this Fe^{2+} doublet in LLZO to the 4-fold-coordinated 24*d* site.

Finally, it should be noted that fits based on four different quadrupole splitting distributions (3 ferric and 1 ferrous) give reasonable χ^2 values of 1.88 at RT and 1.41 at 80 K.

DISCUSSION

XRPD results show that 0.19 pfu Fe^{3+} stabilizes the cubic garnet LLZO phase at room temperature. The measured Fe^{3+} concentration is lower than the intended value of 0.24. This could possibly be the result of Fe_2O_3 loss during grinding whereby some hematite adheres to the walls of the ball mill. Mössbauer spectra show that about 96% of the iron is Fe^{3+} and only 4% is Fe^{2+}. Therefore, Fe^{3+} appears to act similarly as Al^{3+} in LLZO.[3,5,6] It is notable that the X-ray reflections of our Fe-bearing LLZO garnet are broader than those of Al-bearing LLZO garnet (Figure 1). EDX analysis shows that La, Zr, and Fe appear to be uniformly distributed with the same amounts

Table 2. Mössbauer Hyperfine Fit Parameters for Cubic $Li_{7-x}Fe_xLa_3Zr_2O_{12}$ with x = 0.19

	$Fe^{3+}_{tet}(24d)$			$Fe^{3+}_{tet}(96h)$			$Fe^{3+}_{oct}(48g)$			$Fe^{2+}_{tet}(24d)$		
T [K]	IS[c] [mm/s]	QS[d] [mm/s]	*A*[e] [%]	IS [mm/s]	QS [mm/s]	*A* [%]	IS [mm/s]	QS [mm/s]	*A* [%]	IS [mm/s]	QS [mm/s]	*A* [%]
295[a]	0.19	1.05	74	0.19	3.20	19	0.39	0.76	4	1.00	1.70	3
80[b]	0.29	1.07	68	0.25	3.19	22	0.48	0.75	6	1.10	1.80	4

[a]HWHM = 0.28 mm/s. [b]HWHM = 0.26 mm/s. [c]IS = isomer shift (±0.01 mm/s) relative to α-Fe at RT. [d]QS = quadrupole splitting (±0.01 mm/s). [e]*A* = resonant absorption area (±1%) referred to a total resonant absorption area of 100%.

over an analyzed area of about 200 μm^2. Composition data suggests that the garnet crystals are in chemical equilibrium.

The measured Li amounts to about 6.22 pfu, which is less than the theoretical value of 7.00 pfu for end-member LLZO (Table 1). Li deficiency can be explained based on the exchange $Fe^{3+} \leftrightarrow 3Li^+$, which could lead to vacancies at the 24*d*, 48*g*, and 96*h* sites. Geiger et al. (2011), using X-ray single diffraction results obtained on Al-containing LLZO, described 5-fold-coordinated Li located at a 96*h* site. In terms of Al, they argued, based on ^{27}Al MAS NMR spectra and two observed resonances with chemical shift values of 68 and 81 ppm, that Al^{3+} is located at least at two different crystallographic sites. They proposed that the former resonance represents Al at the 24*d* tetrahedral site. Interpretation of the resonance at about 81 ppm is a matter of discussion. Geiger et al. assigned it to Al in 4−5-fold coordination. They also considered the possibility that more than one Al site is represented by this signal. Düvel et al. undertook a systematic ^{27}Al MAS NMR investigation of LLZO garnets containing various concentrations of Al synthesized under different conditions.[6] In garnets with the lowest Al contents, that is less than about Al = 0.30 atoms pfu, they observed resonances at 64 and 78 ppm and at greater Al contents an additional resonance at 81 ppm. They accepted the proposal that the resonance at about 64−68 ppm represents Al at 24*d*. They assigned, however, their observed resonance at 78 ppm to Al that proxys for La and that at 81 ppm to Al (+Li) that proxys for Zr. Al atoms were assigned to crystallographically unspecified tetrahedrally coordinated sites neighboring vacant La and Zr sites. Thus, other than the probable presence of Al at 24*d*, there is uncertainty regarding the exact substitution mechanisms for Al at additional sites in LLZO. Powder neutron diffraction results on Al-containing (ca. 0.61 wt % Al) LLZO reported Li at the 24*d*, 96*h*, and 48*g* sites with Al only at the "nonstandard" garnet octahedral 48*g* site.[11]

In contrast to the work of Geiger et al., Düvel et al. apparently synthesized Al-free "distorted" cubic $Li_7La_3Zr_2O_{12}$ (Düvel, A. Personal communication). Clearly, X-ray powder reflections of their cubic phase are broadened, which could possibly be reflecting nonstoichiometry, small crystal sizes, and/or strain. Such a phase is potentially metastable thermodynamically. It would be interesting to make in situ X-ray powder measurements on such garnets at elevated temperature to test this hypothesis. Aluminum-free cubic LLZO was also synthesized by Xie et al. using acetate salts around 750 °C, and it was observed to be unstable above 800 °C.[13]

The proposal that most, i.e., roughly 66%, Fe^{3+} substitutes for Li^+ at the 4-fold coordinated 24*d* site appears reasonable. Thus, in terms of crystal chemistry, it can be argued that Fe^{3+} incorporation in LLZO is generally similar to that of Al^{3+}. Second, the suggestion that about 22% of Fe^{3+} occurs at a 96*h* site is plausible. The strong distortion of this site could explain the large quadrupole splitting associated with this doublet. This assignment is consistent with the proposal that Al^{3+} could be located at the distorted 96*h* site.[3]

An exact interpretation for the other two weak quadrupole split doublets is more difficult. A small amount of Fe^{3+} (about 5% of the total iron) appears to occur in octahedral coordination. Because the octahedral positions 16*a* are completely occupied by Zr^{4+}, another octahedral position has to be considered. Considering the neutron diffraction study on Al-containing LLZO garnet with reported Al at 48*g*,[11] it is possible that a small amount of Fe^{3+} may occur here as well. We stress, however, that because this Fe^{3+} doublet is so weak, its hyperfine parameters have relatively large errors. The same holds true for the weak Fe^{2+} doublet of 4% intensity. This Fe^{2+} possibly occupies the 24*d* tetrahedral site. In the case of the silicate garnets this is the site where Fe^{2+} normally occurs.[8]

The non-Lorentzian line shapes of the doublets in the Mössbauer spectra may result from local structural variations (electric field gradients) around the Fe cations. This could be caused by different local cation configurations and the presence of vacancies and/or Li delocalization.[3] Reduced crystallinity of the synthetic sample may be another possible reason for the line broadening. Relaxation effects involving Fe can be excluded because the doublet line widths do not change significantly between RT and 80 K.

Aliovalent substitution $Al^{3+}/Fe^{3+} \leftrightarrow 3Li^+$ appears to be important in stabilizing the cubic LLZO phase and also in promoting its high Li-ion conductivity. The latter has yet to be measured for Fe-doped LLZO, and thus, conductivity measurements are being planned.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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