Synthesis, Crystal Structure, and Stability of Cubic Li$_{7-x}$La$_3$Zr$_2$Bi$_x$O$_{12}$

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ABSTRACT: Li oxide garnets are among the most promising candidates for solid-state electrolytes in novel Li ion and Li metal based battery concepts. Cubic Li$_5$La$_3$Zr$_2$O$_{12}$ stabilized by a partial substitution of Zr$^{4+}$ by Bi$^{5+}$ has not been the focus of research yet, despite the fact that Bi$^{5+}$ would be a cost-effective alternative to other stabilizing cations such as Nb$^{5+}$ and Ta$^{5+}$. In this study, Li$_{7-x}$La$_3$Zr$_{2-x}$Bi$_x$O$_{12}$ ($x = 0.10, 0.20, \ldots, 1.00$) was prepared by a low-temperature solid-state synthesis route. The samples have been characterized by a rich portfolio of techniques, including scanning electron microscopy, X-ray powder diffraction, neutron powder diffraction, Raman spectroscopy, and $^7$Li NMR spectroscopy. Pure-phase cubic garnet samples were obtained for $x \geq 0.20$. The introduction of Bi$^{5+}$ leads to an increase in the unit-cell parameters. Samples are sensitive to air, which causes the formation of LiOH and Li$_2$CO$_3$ and the protonation of the garnet phase, leading to a further increase in the unit-cell parameters. The incorporation of Bi$^{5+}$ on the octahedral 16a site was confirmed by Raman spectroscopy. $^7$Li NMR spectroscopy shows that fast Li ion dynamics are only observed for samples with high Bi$^{5+}$ contents.

The Li ion conductivity of LLZO at room temperature is still 1–2 orders of magnitude lower than that of widely used liquid electrolytes or other superionic conductors: e.g., Li$_{10}$GeP$_2$S$_{12}$, and Li$_{1+x}$Al$_{2-x}$Ti$_2$O$_7$ (PO$_4$)$_3$ (LATP).31–33 Hence, there is great interest in further improving its Li ion conductivity by microstructural and crystal chemical engineering.

The Li ion conductivity of cubic LLZO depends on various factors, such as, e.g., (i) amount of mobile charge carriers, (ii) vacancy concentration, (iii) coordination number of Li ions, (iv) strength and length of Li–O bond, and (v) microstructure of samples.34–36 These factors are strongly influenced by the cations that are added to stabilize the cubic $Ia3d$ modification of LLZO. Since Bi$^{5+}$ has a larger ionic radius in comparison to Zr$^{4+}$, the unit-cell parameter $a_0$ for Li$_5$La$_3$Bi$_2$O$_{12}$ (LLBO) is significantly larger in comparison to that of LLZO stabilized with other dopant elements (13.065 vs 12.97 Å).37,38

We decided to study the LLZO–LLBO solid solution, in order to systematically vary $a_0$ and the Li content. Therefore, we synthesized Li$_{7-x}$La$_3$Zr$_{2-x}$Bi$_x$O$_{12}$ (LLZBO) with varying Bi contents ($x = 0.10, 0.20, \ldots, 1.00$) by solid-state synthesis at comparatively low temperatures. By means of X-ray powder diffraction (XRPD) and neutron powder diffraction (NPD) we studied the exchangeability of Zr$^{4+}$ by Bi$^{5+}$ in the LLZO–LLBO solid solution (LLZBO) and its stabilization effect on the cubic...
LLZO structure. The influence of Bi$^{5+}$ on the microstructure was evaluated by scanning electron microscopy (SEM) using backscattered electrons (BSE) and secondary electrons (SE). Energy-dispersive X-ray spectroscopy (EDX) measurements were performed to investigate the chemical composition of samples with regard to La, Zr, and Bi. Raman spectroscopy was applied to obtain information on the site occupation behavior of Bi$^{5+}$. Finally, $^7$Li nuclear magnetic resonance (NMR) line shape measurements were employed to study Li ion dynamics as a function of $a_0$ and composition.

2. EXPERIMENTAL SECTION

2.1. Synthesis. A series of Li$_{1-x}$La$_x$Zr$_{1-x}$Bi$_x$O$_{12}$ garnets with intended mole fractions of Bi ($x = 0.10, 0.20, \ldots, 1.00$) was synthesized by sintering in air. The starting materials were Li$_2$CO$_3$ (99%, Merck), La$_2$O$_3$ (99.99%, Roth), ZrO$_2$ (99.0%, Roth), and Bi$_2$O$_3$ (99.9%, Merck). The reagents were weighed out in their intended stoichiometric proportions with an excess of 10 wt % of Li$_2$CO$_3$ to compensate for the loss of Li$_2$O during sintering. The reagents were mixed in an agate mortar and then cold-pressed into pellets with the help of a uniaxial press. The pellets were put into an alumina crucible. To avoid contamination with Al$^{3+}$ from the crucible, the samples were placed on a pellet of pure LLZO. During the first sintering step, the samples were heated to 850 °C at a rate of 5 °C min$^{-1}$ and calcinated for 4 h. The resulting pellets were then removed from the furnace, ground in an agate mortar, and ball-milled for 1 h in isopropyl alcohol (FRITSCH Pulverisette 7, 80 mm ZrO$_2$ balls). After drying in air, the powder was again cold-pressed into pellets. The sample pellets were again placed on a pellet of pure LLZO and then put into an alumina crucible. The final sintering step was performed at 850 °C for 8 h in air. Small fragments of the sintered pellets were ground in an agate mortar and used for the XRPD, NPD, and NMR investigations.

Material used for the last two characterization methods was stored under Ar. For SEM analysis, polycrystalline chips from the sample pellets were embedded in epoxy resin. The surface was ground and then polished using diamond paste. Relative densities of unaltered samples have been measured by pycnometry. The influence of the Bi$^{5+}$ content and the unit-cell parameters on the theoretical densities has been considered by using theoretical densities obtained from Rietveld refinement of XRPD data. In addition, the presence of extra phases has also been taken into consideration.

2.2. SEM. Scanning electron microscopy investigations were performed using a Zeiss Ultra Plus device to determine the grain size and grain morphology of the samples. In particular, we put emphasis on the investigation of the phase composition and the chemical homogeneity, i.e., the distribution, of La, Zr, and Bi, using a backscattered electron detector (BSE) and energy-dispersive X-ray spectroscopy (EDX) measurements with an acceleration voltage of 20 kV.

2.3. XRPD. X-ray powder diffraction patterns were recorded with a Bruker D8 Advance Da Vinci Design diffractometer with a Lynxeye solid-state detector using Cu Kα$_\text{r}$ radiation to characterize the synthetic products in terms of all phases present and to determine the symmetry of the garnet. Data were collected in the range 10° ≤ 2θ ≤ 80°. A precise determination of the unit-cell parameter $a_0$, separate measurements were performed with addition of a silicon standard with a well-known lattice constant ($a_0 = 5.43088$ Å) to each sample. XRPD patterns were recorded on fresh samples immediately after synthesis as well as on samples that were stored in air for 1 and 3 weeks, respectively. The unit-cell parameter $a_0$ was determined by Rietveld refinement using the program Topas V2.1 (Bruker).

2.4. NPD. Neutron powder diffraction measurements were performed at the Institut Laue-Langevin (ILL) in Grenoble, France. Powder diffraction data were collected at room temperature in constant wavelength mode with $\lambda = 1.594$ Å at the D2B diffractometer. Experiments were performed with a step width of 0.04° in the range 5.8° ≤ 2θ ≤ 159.7°. Data treatment and refinement were carried out with the FULLPROF suite of programs. In all data evaluations, the La, (Zr + Bi), and O atom positions were refined using anisotropic atomic displacement parameters; the atomic displacement factor for the Li1 positions was refined isotropically while that of Li2 was set to 3.5 to avoid large correlations with the occupation factor. Site occupancies on Li sites were then allowed to refine unconstrained and (Zr + Bi) was fixed to full occupation of this site; however, the relative

Figure 1. SEM-BSE images of Li$_{1-x}$La$_x$Zr$_{1-x}$Bi$_x$O$_{12}$ with different magnifications.
amounts of Bi and Zr were allowed to refine freely. The results for Bi and Zr occupancies agree well with those of XRPD refinements.

2.5. Raman Spectroscopy. Raman spectra of the sample pellets were collected at room temperature with a Thermo Scientific DXR Raman microscope using a 10 mW depolarized internal laser light source with an excitation wavelength of 780 nm. The Raman microscope was equipped with a high-resolution grating, allowing the collection of Raman spectra from 50 to 1800 cm$^{-1}$ with a spatial resolution (fwhm) of 2 cm$^{-1}$.

2.6. $^7$Li NMR Lines. For the $^7$Li NMR line shape measurements under static, i.e., nonrotating, conditions the samples were ground in an agate mortar and fire-sealed under vacuum in DURAN glass ampules (ca. 4 cm in length and 0.5 cm in diameter) to permanently protect the powders from any moisture or air. $^7$Li NMR measurements were performed using a Bruker Avance III spectrometer, which was connected to a shimmed cryomagnet (Bruker) with a nominal external magnetic field of $B_0 = 7.04$ T; the $^7$Li resonance frequency $\omega_0/2\pi$ was 116.4 MHz. $^7$Li NMR spectra were recorded with the saturation recovery pulse sequence. In our case, this sequence contained 10 $\pi/2$ pulses to destroy any longitudinal magnetization $M$. After a constant waiting time, the magnetization recovered was flipped into the $(xy)'$ plane via a final $\pi/2$ pulse to detect the free induction decay. Fourier transformation and subsequent phase correction led to the spectra shown in this work.

3. RESULTS

3.1. Crystal Size, Morphology, and Chemical Composition As Seen by SEM and SEM-EDX. After the final sintering step, the sample pellets have a yellow color, the intensity of the color rising with increasing Bi content. Polished samples were examined by SEM-BSE. Figure 1 shows SEM-BSE images of samples with different Bi contents. The grain size of the samples is around 1–3 μm. Single grains show an isometric shape. The Bi concentration does not have a significant effect on the grain size, but an improved densification is noted for samples with higher Bi concentrations. SEM-EDX measurements of La, Zr, and Bi show that
sample compositions for these elements are well in agreement with the intended stoichiometries. Very frequently, a fine-grained phase was found between single LLZBO grains. This phase is interpreted as a mixture of LiOH and Li2CO3, that formed during processing and polishing of samples.

### 3.2. Phase Composition and Unit-Cell Parameters As Seen via XRPD

The XRPD patterns of the Li7−xLa12−xZr2−xBi2O12 (x_int = 0.10−1.00) are shown in Figure 2. The phase compositions of the samples were evaluated by Rietveld analysis. All samples exhibit reflections indicating cubic Ia3d symmetry. For the sample with x_int = 0.10, Rietveld refinement shows about 66% of tetragonal LLZO and 34% of cubic garnet. Some samples show a small peak at 2θ = 28.6° (d = 3.12 Å), which can be attributed to La2Zr2O7, while other samples show a reflection at 2θ = 31.8° (d = 2.81 Å), indicating the presence of small amounts of Li2CO3. If Zr and Bi contents on the octahedral 16a site are allowed to refine freely during Rietveld refinement, the refined Bi contents x_ref obtained from these refinements are well in accordance with the intended Bi contents x_int (see Table 1). Reflections show a relatively broad peak shape, especially at high 2θ angles.

As shown in Figure 3 and Table 1, the unit-cell parameters of LLZBO samples increase with increasing Bi content. For low Bi concentrations, the lattice parameter a_0 is around 13.00 Å and increases up to 13.04 Å for the sample with x_int = 1.00. This observation is in agreement with Vegard’s law, as 6-fold coordinated Bi^{5+} shows an ionic radius of 0.76 Å, which is larger than that of 6-fold coordinated Zr^{4+} (0.72 Å). The correlation between the intended Bi content x_int and the unit-cell parameter a_0 of LLZBO can be expressed by a simple linear regression: a_0 = 0.0494x_int + 12.994. A comparison with other studies on LLZBO shows that the unit-cell parameters obtained in this work are systematically higher; however, the slope of the linear regression is in agreement with other studies on LLZBO and LLZO. The comparatively large unit-cell parameter might not only be attributed to the increase caused by the substitution of Zr^{4+} by Bi^{5+}; it also seems to be related to a partial protonation of LLZBO due to a reaction of the garnet phase with moisture from the air, as this behavior was described for similar compounds as well. This is also indicated by the presence of Li2CO3, as mentioned above, as Li2CO3 can result from the reaction of CO2 from air with LiOH, which is a side product of the protonation of LLZO-type materials.

### 3.3. Stability of LLZBO in Air

To study the stability of LLZBO in air, samples were ground in an agate mortar and stored under air for 1 and 3 weeks, respectively. XRPD measurements including a silicon standard were performed to investigate the formation of secondary phases as well as to determine the unit-cell parameters. The evolution of the unit-cell parameters as a function of the Bi content and the duration of exposure is shown in Figure 3 and Table 1. It is clearly visible that the unit-cell parameters increase if samples are stored under air. This increase is attributed to the protonation of the garnet phase, which was also reported by other studies on LLZO. The protonation reaction also causes the formation of Li2CO3. The presence of small amounts of Li2CO3 in aged samples was confirmed by XRPD measurements due to the presence of an additional reflection at d = 4.16 Å. The peak width of LLZO reflections, especially at high 2θ angles, increases even further in comparison to XRPD patterns of fresh samples; however, attempts to perform a fit using two different LLZBO garnets with different unit-cell parameters did not lead to a significant improvement. Attempts were also made to perform a structural refinement using the I43d model, which was recently reported for protonated Li oxide garnets and LLZO garnets stabilized with certain cations such as Ga^{3+} and Fe^{3+}. The characteristic 310 reflection of space group I43d, which appears at d = 4.10 Å (2θ = 21.6°) for LLZO garnets with a unit-cell parameter of 12.97 Å, would shift to larger d values due to the increasing unit-cell parameters of LLZBO, it might be possible that the additional reflection at d = 4.16 Å (2θ = 21.35°) is related to the phase transformation to the I43d space group. Rietveld refinement showed that, even for strongly protonated LLZBO samples with large unit-cell parameters of 13.08 Å, this characteristic 310 reflection of space group I43d would be located at d = 4.138 Å (2θ = 21.45°). Therefore, the additional reflection at d = 4.16 Å (2θ = 21.35°) is attributed to the 110 reflection of Li2CO3 and not to a LLZBO garnet phase with space group I43d. In addition, the evolution of a small peak at 2θ = 31.8° (d = 2.81 Å) can also be related to Li2CO3. The presence of Li2CO3 was also confirmed by evaluation of NPD measurements as well as by Raman spectroscopy.

### 3.4. NPD

Results of neutron powder diffraction generally confirmed the results obtained by XRPD. Refinement results of 2 different NPD measurements are shown in Figures S1 and S2 in the Supporting Information. As the samples were stored under an Ar atmosphere, NPD samples were only slightly affected by protonation and aging, in comparison to samples from XRPD measurements. The Li2CO3 contents were quantified for all LLZBO samples, yielding about 2% Li2CO3. Small contents of LiOH were found as well. As determined by XRPD, the sample with x_int = 0.10 still shows both tetragonal I4/mcd and cubic Ia3d garnet modifications. In contrast to the evaluation of XRPD data, a model with two different cubic (space group Ia3d) LLZBO phases was used for the evaluation of NPD data of samples with x_int ≥ 0.30, as the data quality and resolution of data obtained from NPD are better than those obtained from XRDP. This model consists of an LLZBO phase with space group I43d. For this second phase only H+ was assumed to occupy 96h sites. The comparatively large unit-cell parameter of LLZBO garnets with different unit-cell parameters did not lead to a significant improvement. Attempts were also made to perform a structural refinement using the I43d model, which was recently reported for protonated Li oxide garnets and LLZO garnets stabilized with certain cations such as Ga^{3+} and Fe^{3+}. The characteristic 310 reflection of space group I43d, which appears at d = 4.10 Å (2θ = 21.6°) for LLZO garnets with a unit-cell parameter of 12.97 Å, would shift to larger d values due to the increasing unit-cell parameters of LLZBO, it might be possible that the additional reflection at d = 4.16 Å (2θ = 21.35°) is related to the phase transformation to the I43d space group. Rietveld refinement showed that, even for strongly protonated LLZBO samples with large unit-cell parameters of 13.08 Å, this characteristic 310 reflection of space group I43d would be located at d = 4.138 Å (2θ = 21.45°). Therefore, the additional reflection at d = 4.16 Å (2θ = 21.35°) is attributed to the 110 reflection of Li2CO3 and not to a LLZBO garnet phase with space group I43d. In addition, the evolution of a small peak at 2θ = 31.8° (d = 2.81 Å) can also be related to Li2CO3. The presence of Li2CO3 was also confirmed by evaluation of NPD measurements as well as by Raman spectroscopy.

![Figure 3. Unit-cell parameters a_0 of as-synthesized LLZBO samples (black dots) and LLZBO samples after storage under air for 1 week (red squares) and 3 weeks (green triangles), respectively.](image-url)
samples obtained by Rietveld refinements of NPD data are shown in Table S1 and Figure S3 in the Supporting Information; the corresponding structural data of selected samples are given in Table S2 in the Supporting Information. Unit-cell parameter values for unprotonated LLZBO samples are similar to values of as-synthesized values obtained from XRPD; while the unit-cell parameters of protonated LLZBO phases are similar to XRPD-derived values of samples that have been stored in air for 1 week. The discontinuity of the unit-cell parameter between samples with \( x_{\text{int}} = 0.70 \) and \( x_{\text{int}} = 0.80 \) might be related to different alteration stages that could not be resolved. Rietveld refinements yield protonated garnet contents between 22% and 34%.

3.5. Raman Spectroscopy. Raman spectra of LLZBO samples are shown in Figure 4.

![Figure 4](image)

Figure 4. Raman spectra of \( \text{Li}_7\text{La}_3\text{Zr}_{5-x}\text{Bi}_x\text{O}_{12} \) samples (\( x = 0.10, 0.20, ... 1.00 \)). Bands at 156, 195, and 1090 cm\(^{-1}\), marked with stars, are attributed to \( \text{Li}_2\text{CO}_3 \). Two vertical lines have been added to highlight the shifting of bands.

In general, the obtained spectra show a good coincidence with other spectra of cubic LLZO stabilized with different aliovalent cations.\(^{16,19,43,49,50}\) In addition to the characteristic LLZO bands, additional bands at 156, 195, and 1090 cm\(^{-1}\) were observed for all samples. These bands can be assigned to \( \text{Li}_2\text{CO}_3 \). Two vertical lines have been added to highlight the shifting of bands.

These observations are well in accordance with results of \(^7\text{Li}\) NMR spectroscopy.

3.6. Static \(^7\text{Li}\) NMR Spectra: Line Narrowing. NMR line shapes of the quadrupole \(^7\text{Li}\) nucleus (spin quantum number \( I = 3/2 \)) are sensitive to both local and long-range Li ion hopping processes. In addition to possible quadrupolar effects, at low temperatures dipolar interactions broaden the spectra; such interactions are averaged with increasing diffusivity of the spin-carrying ions. Thus, by a comparison of line shapes of samples with different compositions at the same temperature, preliminary information on Li ion dynamics can be deduced. For this purpose, static \(^7\text{Li}\) NMR spectra of \( \text{Li}_7\text{La}_3\text{Zr}_{5-x}\text{Bi}_x\text{O}_{12} \) \( (x_{\text{int}} = 0.10-1.00) \) were recorded at three different temperatures at a Larmor frequency of \( \omega_0/2\pi = 116.4 \text{ MHz} \) (see Figures 5 and 6).
exchange. The central line of the sample with \( x_{\text{int}} = 1.00 \) does not change further with increasing temperature; at \( T > 273 \) K the shape of the spectra remains unchanged, demonstrating that the extreme narrowing regime was already reached at 273 K (Figure 5). On consideration of a rigid-lattice line width, \( \nu_{\text{dp}} \), on the order of a few kilohertz, at 273 K (and also higher temperatures) the Li jump rate \( \tau^{-1} \) is estimated to be at least of the same order of magnitude. This is in contrast to the samples with \( x_{\text{int}} > 0.60: \) up to \( T \approx 310 \) K only the rigid-lattice regime is detected (Figure 5). The corresponding mean Li jump rate turns out to be much lower than \( \nu_{\text{dp}} \) and, hence, has no effect on the line width. Hence, significant Li ion dynamics, able to average homonuclear dipole–dipole couplings, is only observed for samples with large amounts of Bi incorporated. The change in rigid-lattice line width with increasing \( x_{\text{int}} \) cf. the samples with \( x_{\text{int}} < 0.60 \), presumably reflects a decreasing Li–Li distance to which \( \nu_{\text{dp}} \) is sensitive.

Li diffusivity averages not only magnetic dipolar but also electric quadrupolar interactions. These effects result from the interaction of the quadrupole moment of the Li nucleus with a nonvanishing electric field gradient at the nuclear site. In contrast to the situation with no electric field gradient, the four Zeeman levels are perturbed so that, in the case of a polycrystalline sample, a powder pattern shows up (Figure 6). Li diffusivity also affects this pattern, leading to averaged quadrupole satellite lines at sufficiently high temperatures. For \( x_{\text{int}} < 0.80 \) the NMR lines reveal distinct patterns (see also the inset shown for the sample with \( x_{\text{int}} = 0.10 \) in Figure 6). The 90° singularities, marked in Figure 6 with dots, point to coupling constants in the order of 60 kHz. The larger the \( x_{\text{int}} \) value, the higher the Li exchange among the electrically different Li sites. Sufficiently fast exchange causes the pattern to vanish. At \( T \) values much higher than those covered in this study, the emergence of a new, fully averaged quadrupole powder pattern is expected, characterized by a reduced coupling constant.

4. DISCUSSION

The main goal of this study is to observe the influence of a partial substitution of \( \text{Zr}^{4+} \) by \( \text{Bi}^{5+} \) in LLZO and the stabilization of the cubic phase. Pure-phase cubic samples were obtained for Bi contents \( x_{\text{int}} \geq 0.20 \), which is consistent with the results of previous studies.\(^2\) It has to be noted that pure-phase cubic garnet samples are obtained by comparatively low Bi contents, as much higher dopant concentrations are needed if other substituting cations, such as \( \text{Ta}^{5+} \) and \( \text{Nb}^{5+} \), are used as substituents for \( \text{Zr}^{4+} \).\(^3\)\(^4\)\(^5\)\(^6\) Rietveld refinement of XRPD data confirms a systematic increase of the unit-cell parameter with increasing \( \text{Bi}^{5+} \) content; additionally, the increase of the unit-cell parameter is partially caused by a protonation of the garnet phase. The increase of the unit-cell parameter due to protonation and the observation of \( \text{Li}_2\text{CO}_3 \) from NPD as well as from Raman spectroscopy indicate that LLZBO is unstable in air. As NPD samples, which have been stored under Ar directly after the synthesis, already show the first signs of protonation, the protonation might already start during the cooling of samples in the furnace. Reactions with \( \text{H}_2\text{O} \) and \( \text{CO}_2 \) from the air cause the formation of \( \text{LiOH} \) and \( \text{Li}_2\text{CO}_3 \), and lead to a protonation of the garnet, which has negative effects on the ion conductivity.\(^4\)\(^4\)\(^3\)\(^5\)\(^6\)\(^7\)\(^8\)\(^9\)\(^0\)\(^4\)\(^5\)\(^6\) Due to the small grain size of the samples and the high porosity of the pellets, both being side effects of the low sintering temperature, the samples provide a large surface for interactions with air. LLZBO samples from this study seem to be very prone to these reactions, as the increase of the lattice parameter was observed after less than 1 week of storage in air. Even samples characterized by XRPD immediately after synthesis show indications for the aging process mentioned above. \( \text{Li}_2\text{CO}_3 \) was partially also documented from NPD measurements of samples immediately after synthesis; however, small concentrations of \( \text{Li}_2\text{CO}_3 \) are hardly observable by XRPD. LLZBO samples stored under Ar were less affected by the aging process, as the unit-cell parameters obtained by NPD, where samples have been stored under Ar, were lower than those obtained from XRPD. However, even NPD samples showed indications for the aging process such as the formation of \( \text{Li}_2\text{CO}_3 \) and the presence of protonated LLZBO. Therefore, the exposure of LLZBO to air should be strictly avoided. In addition, an enhancement of the density of LLZBO samples would also be beneficial, as the surface area of LLZBO grains available for interaction with air would decrease. An increase in the density of LLZBO samples will also have positive effects on the Li ion conductivity.

Results from \(^7\text{Li} \) NMR spectroscopy show that fast Li ion diffusivity for LLZBO is only achieved for high Bi contents. As the samples have been stored under Ar, the samples have not been significantly affected by protonation and the results show a very clear trend as a function of the Bi content. Xia et al. studied the Li ion conductivity of cubic LLZBO with \( x = 0.20 \) and obtained a Li ion conductivity of \( 2.6 \times 10^{-5} \, \text{S cm}^{-1} \).\(^6\)\(^7\)\(^8\)\(^9\) The results from this study indicate that higher Li ion conductivities might be achieved by using samples with higher Bi contents.
Also for Ta-stabilized LLZO, the highest conductivities were reported for Ta contents of 0.60 atoms per formula unit.29 The results of Xia et al. also show that an increase of the density of samples, either by higher sintering temperatures or by the introduction of Al III that acts as a sintering aid, are beneficial for the Li ion conductivity. As stated above, an improved preparation route for LLZBO will be necessary to obtain satisfying electrochemical performances. As Ga III seems to be an even more effective sintering aid for LLZBO in comparison to Al III, it may be worth preparing and studying Ga-bearing LLZBO samples as well.

5. CONCLUSIONS

The cubic modification of LLZO can be stabilized by a substitution of Zr IV with Bi III. Samples prepared by a low-temperature synthesis route show a broad peak shape in XRPD and are sensitive to moisture and CO2 content in air, which leads to the protonation of LLZBO and the formation of LiOH and Li2CO3. This aging has been proven by NPD and Raman spectroscopy as well. The incorporation of Bi into the LLZO structure leads to the evolution of an additional band in the Raman spectrum at ~590 cm⁻¹. 7Li NMR spectroscopy shows that fast translational Li ion dynamics are only observed for samples with large amounts of Bi incorporated.

ASSOCIATED CONTENT

Supporting Information

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