Anomalies in Bulk Ion Transport in the Solid Solutions of Li₇La₃M₂O₁₂ (M = Hf, Sn) and Li₅La₃Ta₂O₁₂

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ABSTRACT: Cubic Li₇La₃Zr₂O₁₂ (LLZO), stabilized by supervalent cations, is one of the most promising oxide electrolyte to realize inherently safe all-solid-state batteries. It is of great interest to evaluate the strategy of supervalent stabilization in similar compounds and to describe its effect on ionic bulk conductivity \( \sigma_{\text{bulk}} \). Here, we synthesized solid solutions of Li\(_{7-x}\)La\(_3\)M\(_2\)Ta\(_2\)O\(_{12}\) with M = Hf, Sn over the full compositional range (x = 0, 0.25...2). It turned out that Ta contents at x = 0.25 (M = Hf, LLHTO) and 0.5 (M = Sn, LLSTO) are necessary to yield phase pure cubic Li\(_{7-x}\)La\(_3\)M\(_2\)Ta\(_2\)O\(_{12}\). The maximum in total conductivity for LLHTO (2 \times 10\(^{-4}\) S cm\(^{-1}\)) is achieved for x = 1.0; the associated activation energy is 0.46 eV. At x = 0.5 and x = 1.0, we observe two conductivity anomalies that are qualitatively in agreement with the rule of Meyer and Neldel. For LLSTO, at x = 0.75 the conductivity \( \sigma_{\text{bulk}} \) turned out to be 7.94 \times 10\(^{-5}\) S cm\(^{-1}\) (0.46 eV); the almost monotonic decrease of ion bulk conductivity from x = 0.75 to x = 2 in this series is in line with Meyer–Neldel’s compensation behavior showing that a decrease in \( E_\text{s} \) is accompanied by a decrease of the Arrhenius prefactor. Altogether, the system might serve as an alternative attractive to Al-stabilized (or Ga-stabilized) Li₇La₃Zr₂O₁₂ as LLHTO is also anticipated to be highly stable against Li metal.

INTRODUCTION

Garnet-type Li₇La₃Zr₂O₁₂ (LLZO), if stabilized in its cubic modification by aliovalent doping, belongs to the most promising solid electrolytes for all-solid-state batteries (ASSBs).\(^{2,3}\) Despite of its high Li-ion conductivity in the mS cm\(^{-1}\) range,\(^{4,5}\) LLZO has attracted great attention because of its nonflammability, high chemical and electrochemical stability, as well as its mechanical robustness.\(^{2,6}\)

Unfortunately, the pure cubic phase (I\(_{a3d}\) no. 230) is thermodynamically not stable at room temperature; at ambient temperature, the tetragonal modification is present (space group: I\(_{41/cd}\) no. 142), which shows a much lower ionic conductivity, see Figure 1a.\(^{7-10}\) The cubic form can, however, be stabilized by the introduction of supervalent cations, such as Ta, substituting, for example, the Zr ions.\(^{5}\) Further elegant doping strategies have been reported as well including F-doping,\(^{11}\) and Ce-doping.\(^{12}\) As a typical example, Li\(_{7-x}\)La\(_3\)Zr\(_{2-x}\)Ta\(_x\)O\(_{12}\) (LLZTO) with x ≈ 0.6 shows ionic conductivities in the order of 1 mS cm\(^{-1}\).\(^{13,14}\) In contrast to Al-stabilized LLZO, where Al\(^{3+}\) occupies part of the Li sites residing on 24d and 96h,\(^{15}\) in LLZTO the Li sublattice remains untouched. In all LLZO compounds, the exact Li content also influences the dynamic properties. As an example, for Li\(_{7-x}\)Ga\(_x\)La\(_3\)Zr\(_2\)O\(_{12}\) an amount of 6.25 (x = 0.25) Li ions per formula unit (pfu) turned out to guarantee high Li ion conductivities with values on the order of 1 mS cm\(^{-1}\) at 20 °C.\(^{13,16}\)

Apart from pure tetragonal LLZO, other tetragonal phases such as Li₇La₃Hf₂O₁₂ (LLHO)\(^{17,18}\) and Li₅La₃Sn₂O₁₂ (LLSO)\(^{19}\) also exist which might be transformed into powerful electrolytes by substitution strategies\(^{2}\) using supervalent cations. Such investigations are expected to be helpful in refining our understanding of ionic conduction in garnet-type electrolytes. Previous studies have shown that Nb, Ta, and Al stabilize the cubic form of the LLSO phase,\(^{17,19,20}\) another investigation showed that Ta is also able to stabilize cubic LLHO\(^{21,22}\) at ambient temperature. To the best of our knowledge, no study so far is available in literature that systematically looked at the change of bulk ionic conductivities of the two solid solutions of Li\(_{7-x}\)La\(_3\)Hf\(_{2-x}\)Ta\(_x\)O\(_{12}\) (LLHTO) and Li\(_{7-x}\)La\(_3\)Sn\(_{2-x}\)Ta\(_x\)O\(_{12}\) (LLSTO) over the full compositional range. Here, we synthesized two series of samples with x values ranging from x = 0 to x = 2.
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Figure 1. (a) Crystal structures of tetragonal Li$_7$La$_3$Hf$_{2-x}$Ta$_x$O$_{12}$ (Li$_7$La$_3$Sn$_{2-x}$Ta$_x$O$_{12}$ view along the c-direction) and cubic Li$_7$La$_3$Hf$_{2-x}$Ta$_x$O$_{12}$ (LLHTO) [Li$_7$La$_3$Sn$_{2-x}$Ta$_x$O$_{12}$ (LLSTO), view along the c-direction]. In tetragonal LLHTO (and LLSTO) the purple dodecahedra correspond to two distinctly coordinated La$^{3+}$ ions (8f and 16d), and the violet octahedra show the coordination spheres of Hf$^{4+}$ (Sn$^{4+}$) residing on 16c. While the blue spheres correspond to octahedrally coordinated Li$^+$ on 8a, the orange ones represent 6-fold coordinated Li$^+$ on 32e and the red ones represent 6-fold coordinated Li$^+$ on 16f. In the illustration of cubic-LLHTO (cubic-LLSTO), the purple dodecahedra reflect the coordination sphere of the La$^{3+}$ ions (A-site, 24e), and the violet octahedra represent the spheres of Hf$^{4+}$ (Sn$^{4+}$) corresponding to the B-site (16c). The blue spheres show tetrahedrally coordinated Li$^+$ (C-site, 24d), while Li$^+$ ions occupying the 96h site are marked by red spheres. (b) PXRD patterns of Li$_7$La$_3$Hf$_{2-x}$Ta$_x$O$_{12}$ (left) and Li$_7$La$_3$Sn$_{2-x}$Ta$_x$O$_{12}$ (right) with x changing in steps of 0.25. At the bottom, the calculated diffraction patterns are also shown. The patterns of samples crystallizing with tetragonal symmetry are highlighted by a different background color. Note that the tiny reflection at 18° (++) seen for Li$_7$La$_3$Sn$_{2-x}$Ta$_x$O$_{12}$ with x = 0.25 did not influence Li$^+$ ionic transport, as a sample without this reflection does show exactly the same conductivity value. (c) Lattice parameters of Li$_7$La$_3$Hf$_{2-x}$Ta$_x$O$_{12}$ and Li$_7$La$_3$Sn$_{2-x}$Ta$_x$O$_{12}$ as a function of the nominal Ta content. The solid lines represent linear fits and reveal Vegard’s behavior. The dashed lines are drawn to guide the eye.

Table 1. Crystal Structures (Space Group and Lattice Parameters a (and c)), Relative Densities $\rho_{\text{rel}}$, bulk Li Ion Conductivities $\sigma_{\text{bulk}}^{\text{at}},$ at Room Temperature, and Activation Energies $E_a$ for the Two Solid Solutions Li$_7$La$_3$Hf$_{2-x}$Ta$_x$O$_{12}$ and Li$_7$La$_3$Sn$_{2-x}$Ta$_x$O$_{12}$

| x    | space group | a (and c)/Å | $\rho_{\text{rel}}$/% | $\sigma_{\text{bulk}}^{\text{at}}$/S cm$^{-1}$ | $E_a$/eV | $\log_{10}(\sigma_b/S$ cm$^{-1}$ K) |
|------|-------------|-------------|------------------------|--------------------------------------------|---------|----------------------------------|
| 0.00 | I4$_1$/a$ar{c}$f | a = 13.09500(58) c = 12.66722(67) | 66 | 2.29 $\times 10^{-4}$ | 0.49(1) | 5.20 |
| 0.25 | Ia3d        | a = 12.95294(18) | 72 | 1.18 $\times 10^{-3}$ | 0.56(1) | 7.10 |
| 0.50 | Ia3d        | a = 12.93323(15) | 74 | 7.04 $\times 10^{-4}$ | 0.63(1) | 8.02 |
| 0.75 | Ia3d        | a = 12.91179(15) | 82 | 1.82 $\times 10^{-4}$ | 0.46(2) | 6.60 |
| 1.00 | Ia3d        | a = 12.89143(17) | 87 | 1.93 $\times 10^{-4}$ | 0.46(2) | 6.55 |
| 1.25 | Ia3d        | a = 12.87337(20) | 82 | 6.01 $\times 10^{-3}$ | 0.49(1) | 6.56 |
| 1.50 | Ia3d        | a = 12.85515(19) | 74 | 9.73 $\times 10^{-3}$ | 0.63(1) | 7.22 |
| 1.75 | Ia3d        | a = 12.84278(11) | 70 | 2.20 $\times 10^{-2}$ | 0.59(1) | 6.98 |
| 2.00 | Ia3d        | a = 12.81884(14) | 59 | 6.62 $\times 10^{-2}$ | 0.67(1) | 7.61 |

| x    | space group | a (and c)/Å | $\rho_{\text{rel}}$/% | $\sigma_{\text{bulk}}^{\text{at}}$/S cm$^{-1}$ | $E_a$/eV | $\log_{10}(\sigma_b/S$ cm$^{-1}$ K) |
|------|-------------|-------------|------------------------|--------------------------------------------|---------|----------------------------------|
| 0.00 | I4$_1$/a$ar{c}$f | a = 13.11917(76) c = 12.56190(87) | 77 | 2.88 $\times 10^{-7}$ | 0.57(1) | 5.61 |
| 0.25 | I4$_1$/a$ar{c}$f | a = 13.06280(68) c = 12.63517(77) | 85 | 5.43 $\times 10^{-3}$ | 0.44(1) | 5.75 |
| 0.50 | Ia3d        | a = 12.90240(30) | 80 | 4.29 $\times 10^{-3}$ | 0.50(1) | 6.85 |
| 0.75 | Ia3d        | a = 12.89057(10) | 76 | 7.94 $\times 10^{-3}$ | 0.46(2) | 6.28 |
| 1.00 | Ia3d        | a = 12.86934(14) | 72 | 3.53 $\times 10^{-3}$ | 0.52(1) | 6.85 |
| 1.25 | Ia3d        | a = 12.85488(14) | 53 | 9.39 $\times 10^{-3}$ | 0.53(2) | 6.48 |
| 1.50 | Ia3d        | a = 12.84028(16) | 51 | 6.38 $\times 10^{-3}$ | 0.57(2) | 7.09 |
| 1.75 | Ia3d        | a = 12.82447(13) | 48 | 1.78 $\times 10^{-3}$ | 0.62(2) | 7.35 |
| 2.00 | Ia3d        | a = 12.81884(14) | 59 | 6.62 $\times 10^{-2}$ | 0.67(1) | 7.61 |

Note: Arrhenius pre-factors $\sigma_b$ are included as well; the error of the logarithmic values is at least in the order of ±0.20.

In the present study, we took advantage of a ceramic sintering approach and systematically investigated the connections between phases, Li content, microstructure and Li$^+$ transport properties by using powder X-ray diffraction (PXRD), scanning electron microscopy (SEM), and broadband impedance and conductivity spectroscopy. The goal was to provide a complete picture of the change in lattice constants, density and Li ion conductivity, i.e., activation...
energies and Arrhenius prefactors, as a function of Li content and Hf(Sn)/Ta site disorder. Strong cation disorder in combination with high macroscopic density yields high ionic conductivities. Importantly, we found conductivity anomalies occurring at certain compositions for which the activation energy increases. This increase is accompanied by a prefactor anomaly which is consistent with the so-called Meyer-Neldel rule.\(^{23,24}\) This compensation rule provides a semiempirical link between the conductivity prefactor and the activation energy.

## METHODS

Li\(_{7−x}\)La\(_x\)M\(_2−x\)Ta\(_x\)O\(_{12}\) garnets with M = Hf, Sn and different compositions (\(x = 0.00, 0.25, 2.00\), in steps of 0.25\(s\)) were synthesized by a solid-state preparation route with subsequent high-temperature sintering. Stoichiometric amounts of Li\(_2\)CO\(_3\) (>99%, Sigma-Aldrich), La\(_2\)O\(_3\) (>99.5%, Merck), Ta\(_2\)O\(_5\) (99%, Sigma-Aldrich), HfO\(_2\) (99%, MaTecK), and SnO\(_2\) (99.9%, Sigma-Aldrich) were mixed by hand. Because of the risk that Li evaporates at high temperatures, an excess of 10 wt % of Li\(_2\)CO\(_3\) was used. The mixtures were intimately ground to prepare pellets with diameters of 10 mm. These pellets were then uniaxially pressed under a force of 5 kN (5 min at 500 rpm (12 times) with breaks for 5 min between the milling periods). Finally, the powders were again milled in a Fritch Pulverisette 7 ball mill for a time period of 2 h (5 min at 500 rpm (12 times) with breaks for 5 min between the milling periods). The samples were then uniaxially pressed under a force of 5–10 kN to prepare pellets with diameters of 10 mm. These pellets were calcined at 850 °C for 4 h; the heating rate to reach the target temperature was 5 °C/min, and after 4 h the pellets were allowed to cool down to room temperature in the furnace. Afterward, the samples were mixed with isopropanol and milled in a Fritsch Pulverisette 7 ball mill for a time period of 2 h (5 min at 500 rpm (12 times) with breaks for 5 min between the milling periods). Finally, the powders were again isostatically pressed (5–10 kN) to prepare pellets (\(d = 10\) mm) for the sintering step. Sintering was carried out at 1100 °C, and the sintering period was 4 h; again, we used a heating rate of 5 °C/min. Importantly, the bottom of the crucible was covered with ZrO\(_2\) powder to reduce possible contamination with Al from the crucible. A so-called “bottom-pellet” with a height of approximately 1 mm, which was prepared from the original material, was put onto the powder. On top of the bottom-pellet, we placed the pressed samples for further sintering. The pellets themselves were covered by a “cap-pellet” to prevent Li loss during sintering. The density was calculated from the unit cell parameters shown in Table 1 and the respective molecular weight of each composition. The relative shrinkage and relative density were determined by the relative shrinkage of the sample diameter and the relative change of the sample dimensions before and after sintering, respectively.

To identify the main phases and any side phases as well as crystal symmetries and unit cell dimensions, powder X-ray diffraction (PXRD) measurements were carried out using a Bruker D8 Advance diffractometer that operates with Cu Ka radiation. Data were collected at angles of 2θ ranging from 10° to 80°. The patterns were analyzed by Rietveld refinement with the program XPert HighScore Plus V3.0 (PANalytical). Scanning electron microscopy (SEM) analysis was carried out by using an SEM ZEISS Ultra 55 device. Small polycrystalline chips, taken from the larger pellets, were embedded in an epoxy resin. The surface was ground and subsequently polished using sand paper with 4000 grit. The surface was coated with a 5–10 nm thin layer of Au/Pd. For the analysis carried out at 15 kV, special attention was paid to extra phases, grain sizes, grain boundaries, and textures. We used both a secondary electron detector (SE) and a backscattered electron detector (BSE) to investigate the ceramic samples.

For the impedance measurements, the sintered pellets with a diameter of approximately 10 mm and a thickness of about 1 mm were used. Au electrodes (100 nm in thickness) were applied on both sides of the pellet utilizing a Leica EM SCD 050 sputter device. Impedance spectra were recorded with a Novocontrol Concept 80 broadband dielectric spectrometer.

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Figure 2. (a) Relative shrinkages and (b) relative densities \(ρ_\text{rel}\) of Li\(_{7−x}\)La\(_x\)M\(_2−x\)Ta\(_x\)O\(_{12}\) (closed circles in red) and Li\(_{7−x}\)La\(_x\)Sn\(_{2−x}\)Ta\(_x\)O\(_{12}\) (open circles in blue) as a function of \(x\). (c) SEM-BSE images of the LLHTO and LLSTO samples prepared. Images refer to two different zoom levels; see the bars indicating either a distance of 0.5 mm or 50 \(\mu\)m. The samples highlighted with a colored frame show the highest ionic conductivities. At the same time, Li\(_{7−x}\)La\(_x\)Hf\(_{2−x}\)Ta\(_x\)O\(_{12}\) with \(x = 1.0\) shows the highest relative density of >85\%.

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covering a frequency range from 10 mHz to 10 MHz; we measured conductivity spectra from 173 to 453 K in steps of 20 K. No optical change of the Au electrodes were observed after the measurements, assuming that at least for temperatures of up to 453 K the electrolyte/Au interface seems to be chemically stable. A QUATRO cryosystem (Novocontrol) controlled the temperature in the sample cell (BDS 1200, Novocontrol). The measurements were carried out under a stream of freshly evaporated N₂ gas to avoid any influence of water or oxygen.

## RESULTS AND DISCUSSION

In Figure 1b, the PXRD patterns of the solid solutions of LLHTO and LLSTO are shown. It can be clearly seen that, in our case, for LLHTO an amount of \( x = 0.25 \) is necessary to fully stabilize the cubic modification. Similar observations were reported by Gupta et al., who managed to stabilize LLHTO with a Ta amount corresponding to \( x = 0.2. \)\(^\text{22} \) We also see that with increasing \( x \) the cubic phase remains the stable polymorph. The corresponding reflections become narrower revealing that the samples have to be characterized by a higher degree of crystallinity and a larger average grain size.

For the LLSTO counterpart, we observe a similar behavior. The only difference compared to LLHTO is that a Ta content of \( x = 0.50 \) is needed to fully stabilize the cubic phase. At \( x = 0.25 \), the corresponding pattern shows that a mixed phase consisting of both tetragonal and cubic LLHTO is present. This finding is different than a previous report; Deviannapoorani et al. showed that an amount of \( x = 0.25 \) is sufficient to stabilize the cubic phase.\(^\text{23} \) Changes in the synthesis conditions may, however, serve as an explanation for this finding as they can cause non-negligible changes in the overall properties of oxide garnets.

The change of the cell parameters, \( a \) and \( c \), as a function of \( x \) of the two solid solutions is shown in Figure 1c. Within the cubic phase regime, we observe Vegard’s behavior, that is, a linearly decreases with \( x \). It decreases from 12.953 to 12.819 Å (LLHTO) and from 12.902 to 12.819 Å in the case of LLSTO; see also Table 1. The origin of the decrease is 2-fold and originates (i) from the replacement of the larger octahedrally coordinated (IV) cations Hf\(^{IV} \) (\( ϱ^{IV} = 0.85 \) Å\(^\text{26} \)) and Sn\(^{IV} \) (\( ϱ^{IV} = 0.83 \) Å\(^\text{26} \)) by the smaller Ta\(^{V} \) cations (\( ϱ^{V} = 0.78 \) Å\(^\text{26} \)) as well as (ii) from the reduction of the Li\(^+ \) content. Since Hf is a bit larger than Sn, the increase of the lattice parameter \( a \) with \( x \) is slightly steeper as compared to the behavior observed for the LLSTO series.

In Figure 2a,b the relative shrinkages and the relative densities of the LLHTO and LLSTO pellets are shown. Data have been determined after the final sintering step. To estimate the behavior illustrated, three samples were each sintered simultaneously. It turned out that the shrinkage of the pellets was very sensitive to their position in the furnace. This sensitivity resulted in non-negligible scattering of the data points. Data shown refer to those pellets that were placed at the same position in the furnace. We see that the relative shrinkage of the pellets because of the final sintering step reaches approximately 15% for \( x = 1.0 \); at this composition, \( ρ_{\text{rel}} \) is given by 87%. Afterward, we recognize a decrease in shrinkage. For LLSTO, we see that at around \( x = 1.0 \) less dense samples as compared to LLHTO were obtained. The largest shrinkage is observed for a Ta content of \( x = 0.50 \). The density of the samples correlates well with the relative shrinkage of those samples. For LLSTO, \( ρ_{\text{rel}} \) reaches about 85% at \( x = 0.25 \). Similar values have been reported by Hamao et al.\(^\text{20} \) Our values are, however, lower than those presented by Deviannapoorani et al., who managed to increase the density of some samples to values as high as 94%\(^\text{25} \).

In Figure 2c, the corresponding SEM-BSE pictures of the two series of samples are shown. In agreement with the result from Figure 2a,b we see that at \( x = 1 \) and \( x = 1.25 \) LLHTO has to be characterized by only a small volume fraction of pores. For LLSTO, on the other hand, relatively dense samples are

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**Figure 3.** (a,b) Nyquist plots of selected samples either crystallizing with tetragonal (a) or cubic symmetry (b). In (a), the complex plane plots of tetragonal Li₁₋ₓLaₓHfO₁₂ and Li₁₋ₓLaₓSnO₁₂ are displayed, and the equivalent circuit to analyze the location curves is also shown. In (b), the bulk semicircles of selected LLSTO and LLHTO samples are presented; see text for further explanation. Apex frequencies and capacitances obtained by evaluating the curves with constant phase elements are also included. (c) Frequency dependence of \( -Z_{\text{IM}} \) and the electric modulus \( M^{\text{IM}} \) of cubic-Li₆.₀La₃Hf₁.₀Ta₁.₀O₁₂ (\( ν = 10^7 \) s\(^\text{−1} \)) yields 2 \( × 10^{-4} \) S cm\(^{−1} \) for LLSTO, with \( x = 0.75 \) the shift of the corresponding peaks toward lower frequencies agrees with a slight decrease in conductivity being slightly lower than 10 \( × 10^{-4} \) S cm\(^{−1} \), see Figure 4a.
obtained for lower contents of $x \leq 0.25$. The images for $x = 0.5$ and $x = 1.0$ look similar, and a significant increase in pore volume is seen for the samples with $x$ being larger than 1. This observation by SEM agrees with the result shown in Figure 2b.

To investigate ionic transport parameters, we carried out broadband impedance measurements, see Figure 3. Exemplarily, in Figure 3b the revealing Nyquist plots of cubic-Li$_7$La$_3$Sn$_{2-x}$Ta$_x$O$_{12}$ for $x = 0.5$ and $x = 1.0$ are shown; the inset shows the corresponding complex plane plot of cubic-Li$_7$La$_3$Hf$_{2-x}$Ta$_x$O$_{12}$ with $x = 1.0$. The plots are constructed by plotting the imaginary part $-Z''_{IM}$ of the complex impedance $Z$ as a function of its real part $Z'_{RE}$; they refer to a temperature $\theta$ of 20 °C. For comparison, in Figure 3a the Nyquist plots of tetragonal Li$_7$La$_3$Hf$_2$O$_{12}$ and Li$_7$La$_3$Sn$_2$O$_{12}$ are displayed.

For the latter two samples, we see a high-frequency semicircle (see Figure 3a) followed by a semicirc in the intermediate frequency range. While the first refers to a bulk electrical relaxation process, the one appearing at lower frequencies mirrors electrical relaxation either in electrical relaxation process, the one appearing at lower intermediate frequency range. While the semicircle (see Figure 3a) followed by a semiarc in the corresponding semicircle seen in the high-frequency region is the response of the second semicircle is given by capacitances $C_P$ and/or polarization at the sample/electrolyte region does not show any obvious changes. In the following, we will mainly focus on bulk properties and their change with composition of the two series studied. Importantly, compared to the tetragonal samples, for cubic-Li$_7$La$_3$Sn$_{2-x}$Ta$_x$O$_{12}$, as well as for the Hf-analogue (see Figure 3a,b), we recognize an immense decrease of the bulk resistance from the MΩ to the kΩ range if $x$ reaches values around 0.75 and 1.0, respectively (see also below). The corresponding semicircle seen in the high-frequency region is characterized by capacitances on the order of few pF, thus clearly pointing to a bulk response.

The same features of several electrical relaxation processes are also found if we take a look at the conductivity isotherms $\sigma(\nu)$. Here, $\sigma'$ denotes the real part of the complex conductivity $\sigma$. As an example, in Figure 4a the isotherms for Li$_7$La$_3$Sn$_{2-x}$Ta$_x$O$_{12}$ with $x = 0.75$ are displayed. This sample shows the highest ionic conductivity in the LLSTO series. In the region of very low frequencies, electrode (or interfacial) polarization is evident that proceeds stepwise. As mentioned above, for LLSTO with $x = 1.0$ any g.b. effects originating from a lower density seem to be overcompensated by the beneficial influence of Sn/Ta cation mixing as the intermediate semicircle does almost disappear. Here, we assume that the grain boundary regions in heavily mixed but less dense LLSTO are less resistive than in nonmixed samples.

Coming back to the location curves shown in Figure 3b, we conclude that the strong increase of $-Z''_{IM}$ observed in the Nyquist plots seen in the low-frequency region represents an interface relaxational process in front of the ion-blocking Au electrodes. Most likely, this process is, again, either caused by direct electrode polarization or by an interphase formed at the Au/electrolyte interface. Visual inspection of the Au/electrolyte region does not show any obvious changes.
nonsuccesful (forward–backward) jump events. For comparison, in Figure 4b the corresponding behavior of the real part, ϵ′, of the complex permittivity ϵ is also shown. Again, in agreement with the Nyquist analyses, the isotherms reveal that the decrease in ϵ′(ν) at low frequencies is mostly likely, caused by polarization effects near the sample/electrode surface as the drop for the isotherm seen at 100 Hz corresponds to permittivities in the order of 10^6. Of course, the different sources for electrical relaxation, especially the one assigned to the bulk response, are also observed when −Z″_IM and M″_IM are plotted versus frequency ν. Here, M″_IM denotes the imaginary part of the complex electrical modulus M. The corresponding spectra, which were recorded at 20 °C, are shown in Figure 3c for the cubic samples with the highest ionic conductivities, that is, for x = 1.0 (LLHTO) and x = 0.75 (LLSTO). The M″_IM peaks (see arrows) appearing in the high-frequency range refer to both the bulk semicircle in the Nyquist representation and to the dc plateau in the ϵ′(ν) plot. Since the amplitude of M″_IM here denoted as M″_max is inversely proportional to 1/ν, bulk responses are more prominent in the modulus representation as compared to those with lower capacitances. In general, while −Z″_IM(ν) pronounces electrical relaxation originating from grain boundaries or interfacial effects M″_IM(ν) is used to shed light on bulk relaxation. Here, for the Hf-bearing sample M″_IM(ν) passes through a maximum at relatively high characteristic frequencies of 10^7 Hz. For the Sn-containing sample, the peaks shift toward lower frequencies, in agreement with the lower ionic bulk conductivity; see also Figures 4a and 5.

For cubic-Li_{6.0}La_{3}Hf_{1.0}Ta_{1.0}O_{12}, a second, much shallower, M″_IM(ν) peak appears at ν = 4 Hz; the corresponding real part, ϵ′, of the complex permittivity ϵ takes values on the order of 10^5. For comparison, for the Sn-bearing cubic samples Li_{7−x}La_{3}Sn_{x}Ta_{1.0}O_{12} the permittivity reaches values of almost 10^6 in this region, indicating a process that is influenced by interfacial effects near or directly in front of the ion-locking electrodes applied. In general, permittivity values of this order of magnitude correspond to capacitances C with values in the nF range.

In addition, for LLHTO (x = 1.0) the ϵ′′(ν) isotherm reveals a plateau at 1 kHz characterized by ϵ′′ = 10^4. This feature is less seen for the LLSTO sample, again indicating that different interfacial processes affect the dielectric properties in this frequency range. We suppose that Sn-containing LLSTO interacts differently with the Au electrode, possibly pointing to a weaker electrochemical stability if in contact with metal electrodes. As a side note, two samples also differ in bulk permittivities. For cubic-Li_{6.0}La_{3}Hf_{1.0}Ta_{1.0}O_{12}, we obtain ϵ′′(ω) values well below 50.33 In the case of the Sn-containing cubic Li_{7−x}La_{3}Sn_{x}Ta_{1.0}O_{12} sample (x = 0.75), we see that ϵ′′ reaches a value of 20 for the M″(ν) peak appearing at 10^6 Hz.

As mentioned above, analyzing the Nyquist curves with appropriate equivalent circuits, see Figure 3, leads to the resistance R_{bulk}, which can be used as a function of both temperature T and composition x. The specific bulk conductivities ϵ′_bulk have been calculated according to ϵ′_bulk = 1/R_{bulk} × (d/A), where d denotes the thickness of the pellets and A is their area. The temperature dependence of ϵ′_bulk is shown using an Arrhenius representation that plots log_{10}(σ'_bulk(T)/T) versus 1000/T, see Figure 5a, and T denotes the absolute temperature in K. In all cases, we observe linear behavior, that is, we calculated the activation energies E_a according to the relationship ϵ′_bulk(T) = σ_0 exp(−E_a / (k_B T)), where k_B is Boltzmann’s constant. The conductivity values obtained for ambient conditions, that is, for θ = 20 °C, as well as the corresponding activation energies E_a are included in Table 1, which also lists the Arrhenius prefactors σ_0. The change of ϵ′_bulk, E_a, and σ_0 for the two series of Li_{6−x}La_{3}M_{x}Ta_{1.0}O_{12} investigated is presented in Figure 5b.

For Li_{6−x}La_{3}Hf_{x}Ta_{1.0}O_{12}, we see that starting from tetragonal symmetry the ionic conductivity increases from 2 × 10^{-6} S cm^{-1} to values being 2 orders of magnitude higher than the initial one. The sample with x = 1.0 exhibits the highest density; at 20 °C, ϵ′_bulk is given as 1.9 × 10^{-4} S cm^{-1}. For larger values of x_i, we notice a decrease again reaching about 8 × 10^{-7} S cm^{-1} for the ordered Li_{6}La_{3}Ta_{1.0}O_{12} sample. The maximum in bulk ionic conductivity for the sample with the largest degree of Hf/Ta site disorder and 6Li pfu corresponds to a minimum in activation energy (0.46 eV). Interestingly, tetragonal Ta-free LLSO also shows a very low ionic conductivity, and its activation energy (0.49 eV) is comparable to that seen for the sample with x = 1.0. However, the corresponding prefactor σ_0 of Li_{6}La_{3}Hf_{x}Ta_{1.0}O_{12} is 2 orders of magnitude lower than that of Li_{6.0}La_{3}Hf_{1.0}Ta_{1.0}O_{12}.

It is worth noting that two conductivity anomalies are seen for the compositions x = 0.5 and x = 1.5; see Figure 5b. In each
explained in terms of order trends have been observed for Al-stabilized LLZO and energetically less favored for long-range ion transport. Similar sublattice; see also ref 19.

We see for cubic $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ samples are higher than expected for this sample; see the dashed line that serves to guide the eye for the continuous change of $\sigma_0$. A small increase in $\sigma_0$ is also seen for $x = 1.5$. Obviously, these Li compositions are energetically less favored for long-range ion transport. Similar trends have been observed for Al-stabilized LLZO and explained in terms of order–disorder phenomena of the Li sublattice; see ref 19.

For the series with Sn, a similar behavior is seen. The maximum in ionic bulk conductivity is reached at $x = 0.75$ ($8 \times 10^{-5}$ S cm$^{-1}$). For $x$ values larger than $x = 0.75$, we observed a continuous decrease in $\sigma'_\text{bulk}$ and an increase in activation energy finally reaching a value of almost 0.7 eV at $x = 2$. If we disregard the anomaly at $x = 1.0$, this increase in $E_k$ is accompanied by a monotonic increase of the Arrhenius prefactor spanning a range of about 1.5 orders of magnitude, a behavior that is again in agreement with the rule introduced by Meyer and Neldel (MN). This empiric compensation rule links the prefactor $\tau_0^{-1}$ of the Arrhenius relation for the ionic Li$^+$ jump rate $\tau^{-1}$ ($= \tau_0^{-1} \exp(-E_k/\kappa B T)$) with the overall activation energy $E_k$ according to $\tau_0^{-1} \approx \tau_{\text{MN}}^{-1} \exp(E_k/\Delta\text{SN})$.

Here, we used $\tau_0^{-1} \propto \sigma_0$ and plotted $\log_{10}(\sigma_0)$ versus $E_k$; see Figure 6. The dashed line in the Meyer–Neldel plot of Figure 6 shows a linear fit excluding the anomalies at $x = 0.5$ and $x = 1.0$ (vide infra). The fit yields $E_{\text{SN}} \approx 0.06$ eV; this value translates into an isokinetic temperature of $T_{\text{iso}} = E_{\text{SN}}/\kappa B \approx 700$ K. We see for cubic $\text{Li}_7\text{La}_3\text{Sn}_2\text{Zr}_2\text{O}_{12}$ that the prefactors are larger for the tetragonal forms. A difference of up to 2 orders of magnitude in the prefactor has recently been also seen if results from tetragonal $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ are compared with those from cubic $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$; see also ref 19.

For the series with Hf, the LLTSO series also reveals two prefactor anomalies (Figure 5c). The samples with $x = 1.5$ and $x = 0.5$, in particular, show activation energies and prefactors that are higher than expected by the dashed line in Figure 5c. Again, the noticeable drop in conductivity for the $\text{Li}_{1-x}\text{La}_3\text{Sn}_2\text{Zr}_2\text{O}_{12}$ sample with $x = 0.5$ is reflected by a somewhat higher activation energy and a considerably larger prefactor, partly compensating the decrease in $\sigma'_\text{bulk}$. The shallow anomaly in $E_k$ and $\tau_0^{-1}$ seen for $x = 1.0$ is hidden in $\sigma'_\text{bulk}$ if values at 20 $^\circ$C are considered; it is, however, seen at temperatures different from $\theta = 20$ $^\circ$C.
The original Ta-free sample crystallizing with tetragonal symmetry, Li$_7$La$_3$Sn$_2$O$_{12}$, shows a very low ionic conductivity and a relatively high activation energy of about 0.57 eV. The latter is higher than that seen for the Hf-analogue. As both tetragonal samples show similar prefactors (see also Figure 6), the higher conductivity in tetragonal Li$_7$La$_3$Hf$_2$O$_{12}$ (note that $\sigma'_{\text{bulk}}$ exceeds that of the Sn-analogue by a factor of 10) turned out to be a direct consequence of the lower activation energy for Li$^+$ transport.

Most interestingly, the Sn-containing sample characterized by $x = 0.25$, which still crystallizes partly with tetragonal symmetry, reveals an unexpectedly high ionic conductivity in the order of $10^{-4}$ S cm$^{-1}$ ($8 \times 10^{-5}$ S cm$^{-1}$). The activation energy (0.44 eV) of this sample, being a mixture of cubic and tetragonal LLSTO, is the lowest one seen in the Li$_7$La$_3$Sn$_2$-$x$Ta$_x$O$_{12}$ series. As the precursor does not change much as compared to that found for $x = 0$ (see Figure Sc and Figure 6), the increase in $\sigma'_{\text{bulk}}$ is again solely due to the lowering of the overall activation energy. Note that this sample shows the highest relative density (85%) of its series. We assume that this sample has to be characterized by a high degree of lattice distortion as the corresponding PXRD reflections turned out to be broader than those seen in the patterns belonging to the pure tetragonal and pure cubic samples.

The above-mentioned anomalies in ionic conductivity are also evident if we use the electric modulus formalism to analyze our data. The corresponding curves may have various origins. Bulk properties and interfacial ion transport is expected to be influenced by sintering procedures, final Li compositions, the defect chemistry, and the element distribution in the ceramics. As an example of how sintering temperatures and sintering periods will influence the total conductivity of garnet ceramics, we refer to Deviannapoorni et al. who reported an increase in total conductivity by more than 3 orders of magnitude, that is, reaching $2.41 \times 10^{-4}$ S cm$^{-1}$ after increasing the density from 75% to 94%. This finding clearly shows that changes in porosity and thus morphology of the samples will greatly influence ion dynamics related to g.b. regions in garnet-type samples. Chen et al. clearly pointed out how the density of pellets does also affect bulk properties. For example, bulk properties may be affected by lattice strain expected to be alleviated the longer the sintering or annealing periods were chosen. As mentioned above, we witnessed a non-negligible interplay of densification and the ratio of cation mixing, most likely affecting both interfacial and bulk ion dynamics.

**CONCLUSIONS**

We synthesized two attractive series of garnet-type ceramics that, depending on the Ta content, crystallize either with tetragonal or cubic symmetry: Li$_7$La$_3$Hf$_2$-$x$Ta$_x$O$_{12}$ and Li$_7$La$_3$Sn$_2$-$x$Ta$_x$O$_{12}$. The samples were characterized by X-ray diffraction to identify the phases formed. We used broadband impedance and conductivity spectroscopy to...
study bulk ion dynamics and correlate the findings with microstructure, that is, relative density, and Li content. The latter was varied from \( x = 0 \) to \( x = 2 \). For the \( \text{Li}_7\text{La}_{3}\text{Sn}_{2-x}\text{Ta}_x\text{O}_{12} \) series, the cubic sample with \( x = 1 \) revealed the highest bulk ionic conductivity \( \sigma_{\text{bulk}} \). Since \( \text{Li}_7\text{La}_{3}\text{Sn}_{2-x}\text{Ta}_x\text{O}_{12} \) is expected to have high electrochemical stability, further improvement of its conductivity could result in an attractive alternative to Al-stabilized \( \text{Li}_7\text{La}_{3}\text{Zr}_{2}\text{O}_{12} \), which is currently discussed to play the major role in future battery applications relying on oxide electrolytes.

For the Sn-analogue, \( \sigma_{\text{bulk}} \) passes through a maximum at \( x = 0.75 \). Interestingly, a mixed sample (\( x = 0.25 \)) being both cubic and tetragonal has to be characterized by a relatively high ionic conductivity almost reaching \( 10^{-4} \text{ S cm}^{-1} \) at 20 °C. The activation energy of this sample, which is characterized by a relatively low Arrhenius prefactor, turned out to be rather low (0.44 eV). Importantly, the relative density of this sample takes the highest value of this series reaching about 85%.

Adjusting the total conductivity in LLZO-based garnets is based on the complex interplay of crystal symmetry, composition, site preferences, and defects on the one hand and morphology as well as interfacial properties on the other hand. Here, we followed the change in bulk ionic conductivity as a function of Li content in the cubic phase regime. In qualitative agreement with the trend predicted by the empirical Meyer–Nelder rule, we observe two conductivity anomalies for which a pronounced decrease in activation energy is accompanied with an increase in the Arrhenius-prefactor. For both series investigated, at \( x = 0.5 \) the ionic conductivity is lower than expected. As we look at bulk ionic dynamics, such a trend can only partly be explained by variations in morphology or porosity of the samples. Here, we find evidence that that order–disorder effects of the Li sublattice are responsible for this observation.

For the \( \text{Li}_{7-x}\text{La}_{3}\text{Sn}_{2-x}\text{Ta}_x\text{O}_{12} \) series, we observe Meyer–Nelder behavior over a large compositional range, that is, an increase in activation energy is accompanied by an increase of the conductivity prefactor \( \sigma_0 \). Comparing results obtained for cubic and tetragonal samples revealed that in garnet-type LLSTO (and in LLTO) with noncubic symmetry the Arrhenius prefactors are by tendency lower than those of their cubic counterparts with cation disorder on the B-site 16\( \alpha \). Most likely, this change is due to different attempt frequencies and/or to a change of the Li\({}^+\) activation entropy that enters \( \sigma_0 \). The highest activation energies and prefactors are found for cubic \( \text{Li}_7\text{La}_{3}\text{Ta}_2\text{O}_{12} \) with no site disorder and a low Li content.

\[ \text{Li}_7 \text{La}_{3} \text{Ta}_{2} \text{O}_{12} \]

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