Observation of Elemental Inhomogeneity and Its Impact on Ionic Conductivity in Li- Conducting Garnets Prepared with Different Synthesis Methods

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1. Introduction

Garnet-type lithium lanthanum zirconate (Li$_7$La$_3$Zr$_2$O$_{12}$ [LLZO]) and its doped derivatives continue to generate interest as solid electrolytes for future solid-state lithium batteries. Most Li-conducting garnets adopt the cubic garnet crystal structure ([La$_3$)$_2$]. However, without extrinsic dopants, LLZO adopts a tetragonal structure ([La$_4$/aLa]) due to its uniquely high Li content, which causes a spontaneous ordering of the Li sublattice.[2–4] This thermodynamically favorable (at room temperature) tetragonal phase has lower ionic conductivity ($\approx$10$^{-6}$ S cm$^{-1}$ at room temperature) compared with the cubic phase ($\approx$10$^{-4}$ – 10$^{-3}$ S cm$^{-1}$).[1,3,6] For this reason, an aliovalent dopant is needed to introduce Li vacancies to stabilize the highly conducting cubic phase.[1,3,7–10] Many doping schemes have been explored, including Al$^{3+}$,[6,7,11] and Ga$^{3+}$[7,12] to dope the Li sublattice, Ni$^{2+}$,[13,14] and Ta$^{5+}$[7,9,14–28] to dope the Zr sublattice, Ca$^{2+}$,[22,29] and other alkaline earths such as Ba$^{2+}$[30] to dope the La sublattice (often used in conjunction with another site dopant), and even recently F$^{-}$[31–33] to dope the oxygen sublattice. Of the many possible compositions of LLZO, Ta-doped LLZO (LLZTO) with formula Li$_{7}$La$_{3}$Zr$_{2}$Ta$_{0.6}$O$_{12}$ (0.2 < x < 1) combines good electrochemical stability with lithium metal[14] and high ionic conductivity ($>1$ mS cm$^{-1}$)[23,34,35] and, by virtue of doping the Zr sites in the garnet structure, does not block sites on the Li sublattice[7] unlike other dopants such as Al or Ga.

Li-conducting garnets are generally synthesized via conventional solid-state reaction (SSR) methods that require high reaction temperatures (in excess of 900 °C) and long reaction times (usually in excess of 8 h) (Scheme 1a).[10,36] Initial blending of oxide precursors is typically accomplished via ball milling for an extended time for mixing, particle size reduction, and to minimize the diffusion distance between individual atomic species.[10,36,37] After the synthesis, further high-energy ball milling is often required to reduce the particle size of the resultant coarse powder to confer greater sinterability.[10] In many cases, multiple milling and calcination steps are used to ensure full intermixing of atomic species.[10] Each of these steps has a large time cost in addition to requiring substantial thermal and
mechanical energy input. For these reasons, many less energy intensive synthetic methods have been explored to produce LLZO, often with the added goal of achieving smaller particle sizes in the as-synthesized material.[10,36]

Our group has devoted substantial efforts to the synthesis of nanostructured LLZO using alternative methods to SSR (Scheme 1a). The variety of synthesis methods has enabled a systematic investigation of the role of synthesis-related parameters, such as reaction temperature and particle size, on the resulting sintering and electrolyte properties of LLZO, the focus of the work reported herein. To understand these relationships, we must first briefly describe the synthetic methods used in this study.

Sol–gel and combustion methods are frequently used to prepare ceramics at lower temperatures than those needed for SSR. We recently demonstrated a non-aqueous polymer (NAP) combustion method to synthesize garnet nanopowders at 700 °C,[38] wherein metalorganic precursors are dissolved in a non-aqueous solution with a polymer additive, and subsequently dried and combusted to yield nanosized garnet powder (Scheme 1b). Some benefits of this polymer combustion method include more controlled reactivity compared with nitrate-based sol–gel methods as well as improved stability of the sol against hydrolysis over extended time frames.

In addition, we have developed several molten salt synthesis (MSS) approaches for Ta-doped LLZO (Scheme 1c).[39–42] Recently, we investigated[40] the effect of Lux–Flood basicity on the formation temperature of LLZTO. The Lux–Flood acid–base theory considers the acidity or basicity of oxides, wherein an acid is a $\text{O}^{2-}$ acceptor, and a base is a $\text{O}^{2-}$ donor.[43,44] By increasing the Lux–Flood basicity of the melt components, the formation temperature of LLZTO can be successively reduced from 900 to 550 °C.[40] In this case, three categories of salt medium were used: non-basic halide salts (LiCl–KCl, chloride-MSS), a partially basic mixture of halide and hydroxide salts (LiCl–LiOH, mixed-MSS), and a highly basic mixture of LiNO$_3$–Li$_2$O$_2$–LiOH (highly basic MSS (HB-MSS) as well as a modified HB-MSS method (mHB-MSS) with different ratios of these salt components). Using a basic MSS method, sintered LLZTO ceramics with a relative density greater than 90% and a room temperature total ionic conductivity up to 0.61 mS cm$^{-1}$ were demonstrated.

We also showed that an extension of this MSS approach could be used to prepare LLZTO from pyrochlore-type lanthanum zirconate nanocrystals, which were doped to contain La, Zr, and Ta with a nominal composition of La$_{2.4}$Zr$_{1.12}$Ta$_{0.48}$O$_{7.04}$.[41] Using this approach (which we call pyrochlore-to-garnet [PG-MSS]), LLZTO powders could be obtained in the mHB-MSS medium at synthesis temperatures as low as 400 °C, or blended with a Li source and reactively sintered to form dense garnet electrolyte membranes due to the convenient containment of all cationic species besides Li in the pyrochlore powder.[41]

From all of these studies, we found that in each case, garnet electrolytes with high relative density (>90%) and ionic conductivity (>0.5 mS cm$^{-1}$) can be obtained when the processing was optimized. On the other hand, a range of values of ionic conductivity were observed, with some samples or synthesis methods apparently able to produce electrolytes with higher conductivity. Even between highly similar synthesis methods, differences in
ionic conductivity arise. For example, the maximum ionic conductivity from sintered LLZTO obtained from the HB-MSS process depended strongly on the ratios of LiNO₃, Li₂O₂, and LiOH comprising the molten salt reaction medium used to synthesize the powders; depending on the composition of the melt, the maximum room temperature total conductivity obtained varied from 0.35 up to 0.61 mS cm⁻¹.[40] Interestingly, the presence of elemental inhomogeneity, characterized by variation in the local Ta and Zr content of individual grains of LLZTO, could be observed in one case.[40] Scanning electron microscopy (SEM) backscatter electron (BSE) imaging and energy dispersive X-ray spectroscopy (EDS) revealed the presence of bright grains with higher Ta content, which were indistinguishable from the surrounding grains in normal secondary electron images, and the observed deviation in actual local composition was correlated with lower ionic conductivity. The appearance of grains of different composition in sintered LLZTO strongly implies that some variation in composition exists in the as-synthesized powder, which serves as a starting point for analysis. Furthermore, the sinterability and ionic conductivity of the LLZTO samples were observed to vary depending on the synthesis method used.[40]

The variability in performance metrics such as ionic conductivity is apparently not limited to our samples synthesized by different methods and at different temperatures, but is also reflected in the large body of scientific literature on Ta-doped LLZO. Comparison of various results from the literature (see Table S1, Supporting Information) shows that 1) the “optimal” Ta-doping level (i.e., “x” in Li₇₋ₓLa₃Zr₂₋ₓTaₓO₁₂) is not agreed upon in the literature, and 2) that there are considerable differences in maximum total ionic conductivity between the various examples listed. For example, Wang and Lai obtained LLZTO with a conductivity between 0.69 and 0.73 mS cm⁻¹ for 0.2 < x < 0.3.[23] Similarly, Yi et al. obtained a high conductivity of ≈1 mS cm⁻¹ for x = 0.3.[24] On the other hand, the results of Li et al. showed a poor ionic conductivity of 0.28 mS cm⁻¹ for x = 0.2, and a high conductivity up to 1 mS cm⁻¹ for x = 0.6.[23] Finally, single crystals of LLZTO showed ionic conductivities of 1.1 and 1.3 mS cm⁻¹ for x = 0.4[33] and 0.5[134] respectively. It is unexpected that Ta-doping levels in the range of 0.2 < x < 0.3 would produce cubic garnets with high conductivity, as the critical Ta-doping amount was demonstrated in one study to be in the range of 0.4–0.5 mol per formula unit (PFU).[33] One plausible explanation for these differences is the incorporation of Al as co-dopant, either intentionally or adventitiously through contamination from sintering crucibles, into the Ta-doped garnet phase, which may explain why studies using lower Ta content still produce cubic garnets with high conductivity. While some researchers intentionally add some Al₂O₃ to LLZTO to serve as a sintering aid,[15] the works of Xia et al.[45] and Badami et al.[24] indicate that Al₂O₃ can also have deleterious effects on conductivity and performance. However, Li et al. also observed some Al incorporation into their garnet electrolytes and still obtained a maximum conductivity at a high Ta content (x = 0.6) rather than at lower levels.[23] Clearly, there are many synthesis or processing variables that can affect the performance of Ta-doped LLZO electrolytes besides just the nominal composition.

In this work, we aim to examine some of the synthesis-related factors that may contribute to the differences in performance of garnet electrolytes by systematically characterizing the various LLZTO powder samples discussed herein. SEM, transmission electron microscopy (TEM), or scanning TEM (STEM) with EDS are used to understand the morphology and composition of individual particles, whereas XRD and, in some cases, X-ray pair-distribution function (PDF) analysis are used to understand the bulk crystallinity of the samples and, for the first time, compare the structural properties of identical LLZTO compositions prepared with vastly different synthetic approaches and temperatures. Then, we examine the effect of elemental inhomogeneity, which we define as local deviations in actual Zr/Ta mole ratio, as another factor that contributes to variation in ionic conductivity. While other factors such as grain size[46,47] and chemical inhomogeneity arising from impurity phases[48] may also influence electrochemical properties such as critical current density and interfacial impedance, these are not explored in detail in this work. We show that the various synthesis and processing-related variables in each of the aforementioned preparation methods play a role in these compositional variations, and that even LLZTO synthesized via conventional, high-temperature SSR can exhibit substantial variability in local composition depending on synthesis and sintering parameters. However, by improving reagent mixing and using LLZTO powder with low agglomeration and small particle size distribution, the compositional uniformity of sintered garnet electrolytes can be improved. The correlation between inhomogeneity present in sintered LLZTO and reduction in ionic conductivity is explored.

These results provide evidence that in addition to other variables known to affect the ionic conductivity of garnet electrolytes, such as relative density[49] and Li content[9] (or Li₂O loss[15]), the compositional homogeneity of the final sintered ceramic can influence the ionic conductivity of solid garnet electrolytes.

2. Results and Discussion

2.1. Ionic Conductivity Comparison of Li₆₋₄La₃Zr₁.₄Ta₀.₆O₁₂ Synthesized by SSR, Combustion, and MSS

For comparison with the LLZTO synthesized in our previous works via NAP combustion synthesis,[38] MSS,[40] and PG-MSS,[41] LLZTO of the same nominal composition (Li₆₋₄La₃Zr₁.₄Ta₀.₆O₁₂) was prepared via conventional SSR and sintered using the same approach to produce a standard sample set for comparison. Three types of SSR LLZTO were synthesized to explore the effect of synthesis temperature and degree of mixing of the various reactants on the properties of the resultant material. To examine the effect of repeated milling and calcination steps on the composition, two sample sets of LLZTO were synthesized by calcination at 950 °C for 8 h, one with a single reaction step (1 x SSR₉₅₀) and the second with intermediate ball milling before a second calcination (2 x SSR₉₅₀) at 950 °C for another 8 h. For one set of these SSR samples, pre-ball-milled Ta₂O₅ and nanosized ZrO₂ powders were used to examine the effect of using nanosized reagents. For the other set, bulk Ta₂O₅ and ZrO₂ were used. These samples are prefixed with “N” or “B” to denote nanosized and bulk reagents, respectively (e.g., “N-1 x SSR₉₅₀” and “B-1 x SSR₉₅₀”). For comparison, LLZTO was also synthesized in a single step from bulk reagents by calcination at 1000 °C for 8 h (1 x SSR₁₀₀₀).

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The synthesis conditions for these samples along with the other samples referenced from our previous works are summarized in Table 1, along with the naming nomenclature used to refer to the various samples discussed herein. Details of the sintering conditions can be found in Table S1, Supporting Information. X-ray diffraction (XRD) patterns of the as-synthesized SSR LLZTO powders (along with relevant MSS and NAP combustion LLZTO powders discussed herein, ordered by increasing synthesis temperature) are shown in Figure S1, Supporting Information, and the example SEM images of the as-synthesized SSR LLZTO samples before ball milling for particle size reduction are shown in Figure S2a–c, Supporting Information.

As a starting point for comparison, the ionic conductivity of SSR LLZTO samples was evaluated. The temperature dependence of ionic conductivity was also evaluated between 273 and 343 K for one 1×-SSR1000 and one 2×-SSR950 sample to determine the activation energy of Li-ion conduction, which, for each case, was 0.41 eV per atom, in line with the literature values presented in Table S1, Supporting Information. These measurements are presented in Figure S3a–c, Supporting Information.

Table 1. Summary of synthesis methods discussed herein including SSR, MSS, and non-aqueous combustion synthesis for Li6.4La3Zr1.4Ta0.6O12 garnet powders. The room temperature lattice (where measured, \(\sigma_{\text{lattice}}\)) and total (\(\sigma_{\text{tot}}\)) ionic conductivity for the specific sintered garnet samples analyzed in this work are given in units of mS cm\(^{-1}\).
Information. In addition, SEM fracture surface images of each of these samples are shown in Figure S2f,g, Supporting Information, showing primarily transgranular fracture and high relative density. Nyquist plots used to determine room temperature ionic conductivity for the new samples prepared in this study are shown in Figure S3, Supporting Information, and details used to determine ionic conductivity for these samples are contained in Table S2, Supporting Information. The synthesis and sintering conditions, relative density, total room temperature ionic conductivity, and (where measured) activation energy of these samples are shown in Table S1, Supporting Information, along with relevant metrics cited from our previous combustion and MSS specimens. Finally, other examples of properties of Ta-doped LLZO obtained from various synthesis and processing methods from the literature are included in Table S1, Supporting Information, for comparison.

The highest total ionic conductivity obtained from our samples is that of the $1 \times -SR_{1000}$ sample at 0.71 mS cm$^{-1}$, although the best result from MSS (mHB-MSS)$^{[40]}$ has a comparable total conductivity of 0.61 mS cm$^{-1}$. However, there are still substantial variations in the total ionic conductivity between these various samples, even of similar relative density, especially when comparing the HB-MSS and $1 \times -SR_{1000}$ (93.4% and 93.0% relative density, respectively) samples, where the $1 \times -SR_{1000}$ sample has more than double the room temperature ionic conductivity. As all the samples described herein and in our previous works$^{[38,40,41]}$ were sintered in a manner to minimize Li$_2$O loss using the same approach, the effect of variation of Li content due to evaporation should be minimal. Furthermore, as many samples were sintered for each method, the samples with the highest room temperature ionic conductivity are considered approximately optimized, such that Li$_2$O loss is minimal. Therefore, another effect must explain the large discrepancy in performance between these various LLZTO samples.

2.2. Observation of Elemental Inhomogeneity in LLZTO Garnet Powders

Beginning with the LLZTO synthesized at low temperatures (HB-MSS, mHB-MSS, and PG-MSS LLZTO powder), microscopic analysis was performed via S/TEM due to the generally small particle sizes produced by these synthesis methods. We note that all of these powders were synthesized in the same molten salt medium (Table 1) but with different salt ratios, and, in the case of PG-MSS, a different precursor (i.e., doped pyrochlore nanocrystals instead of metal salts/oxidic reagents). Figure 1a,b shows a low magnification TEM image and corresponding electron diffraction (ED) pattern of an HB-MSS fused particle, showing that the approximate minimum dimensions of individual primary particles are on the order of 200–300 nm, and that this composite particle is a single crystal. Figure 1c,d shows low magnification TEM images of mHB-MSS particles, and Figure 1e,f shows low magnification high-angle annular dark field STEM images of PG-MSS samples. In each case, the particles are submicrometer but generally have dimensions above 100 nm. Other examples of HB-MSS particles are shown in Figure S4, Supporting Information, with corresponding ED patterns, indicating that these particles are composed of at most a few fused nuclei.

In addition, EDS was performed to understand the composition of individual garnet particles from the HB-MSS, mHB-MSS, and PG-MSS methods. Processed EDS spectra (processing methods outlined in the Supporting Information) of sets of individual LLZTO particles for these three MSS samples are shown in Figure 2a–c, respectively, with Ta M, Zr L, and La L X-ray signals indicated (each spectrum corresponds to one particle/particle agglomerate such as in the examples presented in Figure 1). All spectra were smoothed, background subtracted via a polynomial fit, and normalized to the highest intensity La L X-ray peak at $\approx 4.6$ keV. The Ta M and Zr L peaks can be observed to vary considerably on a particle-by-particle basis. To approximately determine the composition of individual particles, EDS spectra of Li$_{3-x}$La$_3$Zr$_{2-x}$Ta$_x$O$_{12}$ (0.2 < x < 1) were simulated and used to generate a regression based on the Ta M to Zr L peak ratio as a function of composition, which was then applied to the processed experimental EDS spectra (see Figure S5, Supporting Information). Figure 2j shows the distribution of peak ratios as a kernel density, showing standard deviations greater than...
0.14 mol PFU in each sample set. Curiously, the HB-MSS sample shows less inhomogeneity than the mHB-MSS sample despite the higher ionic conductivity of the latter sample,[40] which will be discussed later. We would like to note that the PG-MSS powder examined via STEM was prepared under slightly different conditions as those used to prepare sintered LLZTO for ionic conductivity evaluation (STEM-EDS sample: 500 °C, 3 h reaction time; sintered sample: 550 °C, 1 h reaction time, see Table 1), but is included to show that variability in composition occurs in LLZTO derived from this method as well. Despite the slightly lower reaction temperature for the PG-MSS sample characterized with EDS compared with the HB-MSS sample (500 vs 550 °C), the degree of inhomogeneity is comparable, likely due to the better mixing of La, Zr, and Ta afforded by utilizing doped pyrochlores as reagents.

The same EDS data processing approach discussed earlier was applied to the SEM-EDS spectra of the chloride-MSS (Figure 2d) and SSR samples (Figure 2e–i). Despite the higher SSR reaction temperatures, variation in the Ta content can still be readily observed (Figure 2k). Furthermore, in the case of both N-1-SSR950 and B-1-SSR950 LLZTO (shown as the green solid and dotted lines, respectively, in Figure 2k), the standard deviation of the Ta content substantially exceeds that found in the low-temperature MSS LLZTO samples. This result is somewhat surprising as the general assumption is that the high reaction temperatures used in SSR will promote enough solid-state diffusion to drive the whole ensemble of reagents to a uniform final product. However, using either a second calcination with an intermediate ball-milling step (for better intermixing of individual atomic species) or a higher calcination temperature appears to result in better compositional uniformity. It is notable that the use of ZrO2 and Ta2O5 with smaller particle sizes (i.e., N-1-SSR950 and N-2-SSR950, indicated by the green solid and blue solid lines, respectively, in Figure 2k) seems to improve compositional homogeneity after the second calcination. In the case of a single higher temperature calcination (1-SSR1000), the standard deviation of the Ta content is fairly low and has a tight distribution,
and if one outlier sample is excluded, the standard deviation is even lower than for the N-2 × -SSR950 Sample (0.09 mol Ta PFU vs 0.107 mol Ta PFU). The SSR procedures used in this work were chosen based on commonly used parameters from the literature (some examples in Table S1, Supporting Information). This implies that more intensive milling, higher temperatures, and/or longer reaction times may be necessary to ensure compositional uniformity during synthesis than are commonly used, and as exemplified by the 1 × -SSR1000 sample, a higher temperature calcination with overall lower reaction time may be a more effective strategy than using a minimal reaction temperature and extended reaction time.

2.3. Crystal Structural Characterization of LLZTO Garnet Powders

One clue to the effect of synthesis method on the properties of LLZTO is the observation of peak broadening in the XRD patterns, especially for LLZTO synthesized at lower temperatures (Figure S1, Supporting Information). Comparing the various XRD patterns from the samples investigated herein reveals that the full-width half-maximum (FWHM) of the Bragg reflections varies considerably (Figure 3, and Table S3, Supporting Information). Although Scherrer\(^\text{[50,51]}\) broadening is one potential explanation due to the smaller particle sizes of LLZTO prepared by MSS compared with SSR, it generally only occurs for crystallites below \(\approx 0.2 \mu m\). For the HB-MSS samples, ED measurements indicate that most of the particles examined are either single crystals or agglomerates of only a few nuclei and are generally between 0.2 and 1 \(\mu m\) in size (Figure S4, Supporting Information). Furthermore, the mixed-MSS powder synthesized at 700 °C in our previous work\(^\text{[49]}\) presented as large faceted crystals (most likely single crystals) on the order of tens of micrometers, but exhibits broadened peaks relative to SSR LLZTO much like the lower temperature MSS samples, indicating that crystallite size effects cannot solely account for peak broadening.

Another possible explanation, supported by the compositional variations in the EDS data (Figure 2), is coexistence of multiple garnet phases with slightly different composition, as the lattice constant of LLZTO is expected to decrease with increased Ta content following Vegard’s Law.\(^\text{[3]}\) A binary mixture of two LLZTO compositions with deviations of roughly \(\pm 15\%\) in terms of moles Ta PFU has been observed with high-resolution synchrotron XRD.\(^\text{[9]}\) Therefore, it can be expected that if multiple garnet phases with the same crystal structure and only slightly varying lattice parameter coexist in a single sample, Bragg reflections will be observed at approximately the same average positions but with a broadening proportional to the distribution of lattice parameters present. To further understand the origin of the XRD peak broadening, X-ray PDF analysis was performed to complement the Bragg diffraction data. As the PDF is derived from total scattering measurements, its signatures are useful for understanding the atomic structure of materials with crystalline defects, small crystallites, and amorphous phases.\(^\text{[52,53]}\)

Figure 4 shows PDFs for LLZTO samples synthesized by several MSS methods and SSR, covering a synthesis temperature range of 550–950 °C. While all PDFs share generally similar features, the finer features particularly in the range of \(5 < \theta < 10\) and \(18 < \theta < 22\) Å (indicated by the boxed regions in Figure 4) of the mixed-MSS, chloride-MSS, and 2 × -SSR950 samples are much clearer than for the mHB-MSS method. From the calculated partial PDFs (Figure S6, Supporting Information), the correlations in the 5–10 Å region mostly correspond to the second and third nearest-neighbor La–La distances, with Zr–Zr and Ta–Zr correlations contributing to the shoulder at \(\approx 6.5\) Å, and correlations between La and Zr/Ta or Ta–Ta/Ta–Zr/Zr–Zr dominating the finer features from \(\approx 8.5\) to 10 Å. This region between 18 and 22 Å, features originating from these some correlations contribute to most of the peaks, which appear to be substantially broadened in the case of mHB-MSS LLZTO synthesized at a lower temperature.

The PDFs were refined based on the \(La_3\text{Li}_{6.4}La_3Zr_{1.4}Ta_{0.6}O_{12}\) structural model reported by Logéat et al.\(^\text{[3]}\) Refinements showed reasonably good fits to the structural model, with goodness of fit, \(R_w\), between 14% and 28% (Figure S7 and Table S4, Supporting Information). Notably, the correlations from 5 to 10 and 18 to 22 Å mentioned previously are well fit by the refinement, thus confirming the good crystallinity of the high-temperature samples. The mHB-MSS fit is the poorest (\(R_w \approx 28\%\), due to the broadening of features relative to other samples. From the EDS analysis in Figure 2, the N-2 × -SSR950 sample has relatively low compositional variation and, from the PDF analysis, exhibits much more well-defined features (i.e., less peak broadening) than the other LLZTO samples (particularly the lower temperature MSS sample). The lower elemental inhomogeneity of the N-2 × -SSR950 sample and good fit

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**Figure 3.** XRD patterns of LLZTO from a) the various powder samples investigated in this work with synthesis temperature indicated and reference generated according to structure in Logéat et al.\(^\text{[3]}\) plotted between \(30° < 2\theta < 35°\) (wider scans plotted between \(15° < 2\theta < 60°\) in Figure S1, Supporting Information), and b) the HB-MSS and 1 × -SSR1000 samples to highlight the differences in peak FWHM. There are substantial differences in peak breadth for the reflections noted between different samples, especially when comparing LLZTO synthesized at low versus high temperatures (PD indicates N-1 × -SSR950 and N-2 × -SSR950 samples, prepared from pre-ball-milled \(Ta_2O_5\) and nanosized \(ZrO_2\) rather than bulk reagents).

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quality from the PDF refinement implies that elemental inhomogeneity may be an explanation for the broadening in the PDF data. On the other hand, the fit quality is similar between the N-2×-SSR950 and chloride-MSS samples (≈14% difference), but the latter sample has a 30% greater standard deviation in the Ta content (0.139 vs. 0.107 mol Ta PFU for chloride-MSS and N-2×-SSR950, respectively). Furthermore, the XRD patterns for the various SSR samples shown in Figure 3 are difficult to distinguish based on peak broadening but possess substantially variable Ta content (Figure 2), whereas the HB-MSS, mHB-MSS, and PG-MSS samples have less inhomogeneity than both 1×-SSR950 samples (Figure 2) but have broader XRD peaks (Figure 3). Finally, the broadening effect in the PDF data is most obviously correlated with the synthesis temperature used, with the best fit resulting from the highest synthesis temperature (950 °C) and the worst fit resulting from the lowest synthesis temperature (550 °C). Therefore, there may also be a different cause for the broadening in the PDF and XRD data, which is unique to the lower synthesis temperatures used for several of the MSS LLZTO samples and is distinct from elemental inhomogeneity.

Another possible explanation for these broadening effects is some form of crystalline defect, namely, paracrystalline disorder resulting from crystalline defects that cause deviation from perfect long range order. In a Bragg diffraction experiment, such disorder manifests as an increase in peak FWHM as a function of scattering vector Q (or scattering angle in ° 2θ) on top of other fixed broadening mechanisms such as increased K_d/K_p splitting. To investigate this effect in our LLZTO samples, the FWHM as a function of Q is determined for several Bragg reflections for the XRD datasets in Figure S1, Supporting Information, with the trend of peak FWHM plotted in Figure 5a. Clearly, different LLZTO samples have substantially different degrees of broadening as a function of Q, indicating that varying degrees of crystalline disorder are present. In Figure 5b, the peak ∆FWHM (° 2θ) is plotted as a function of synthesis temperature. A clear trend can be observed wherein higher synthesis temperatures result in narrower peaks (Figure 3 and Table S3, Supporting Information) and less broadening as a function of scattering angle (ΔFWHM). This result is intuitive, as a higher reaction temperature naturally will result in faster solid-state diffusion and easier crystallization. Considering these results, the best explanation of the different degrees of broadening in the PDF data in Figure 4 is also degree of crystalline disorder rather than inhomogeneity. Two samples (circled in Figure 5b) are exceptions to the general trend of temperature and peak broadening, namely, the sample from PG-MSS at 550 °C and from NAP combustion synthesis at 700 °C. In the first case, the containment of La, Zr, and Ta in a single, doped pyrochlore phase seems to help reduce diffusion distances and may allow for better crystallinity to be obtained despite the lower synthesis temperature. In the second case, the initial molecular mixing of precursors in solution is expected to have a similar effect. Finally, there is no correlation observed between the elemental inhomogeneity in a powder sample (where measured, see Figure 2) and the degree of peak broadening in the corresponding XRD patterns (Figure 5c). Therefore, the peak broadening observed in many of the XRD and PDF data can be primarily attributed to the degree of crystalline disorder in the powder sample and is strongly correlated with the synthesis temperature, rather than compositional heterogeneity. Conversely, elemental inhomogeneity contributes little to the signals detected in structural characterization methods, as substantially different degrees of peak broadening occur for samples with comparable levels of inhomogeneity (Figure 5c, e.g., B-1×-SSR950 and mHB-MSS). With this in view, structural characterization, while useful in other respects, is not the best tool to assess uniformity of composition in the LLZTO system, as variation in composition is difficult to

Figure 4. Experimental synchrotron X-ray PDF plots of various LLZTO samples from a variety of synthetic methods (spanning synthesis temperatures between 550 and 950 °C) plotted between 1 and 30 Å, showing that the sharpness of features in the various samples is greatest for samples synthesized at higher temperature.
separate from other effects that contribute more to signal variations in Bragg diffraction and even PDF analysis.

2.4. Observation of Elemental Inhomogeneity in Sintered Garnet Solid Electrolytes

The XRD and PDF results of the LLZTO powders demonstrate that the presence of crystalline disorder is related to the synthesis method and temperature used, with more disorder generally appearing in lower temperature synthesis methods. However, the powders are further densified with high-temperature sintering for ionic conductivity measurements, which can also improve the crystallinity. Figure 6 shows the XRD patterns of several LLZTO powder samples (low-temperature mHB-MSS, high-temperature chloride-MSS, and high-temperature SSR) before (Figure 6a) and after (Figure 6b) sintering at 1200 °C for between 2 and 4 h. The results show that while the XRD patterns of the as-synthesized powders have varying degrees of peak broadening, the XRD patterns of the pellets are nearly indistinguishable after sintering. In fact, the ΔFWHM (measured in the same way as powder samples in Figure 5) for these three sintered samples are 0.08, 0.08, and 0.09, respectively, indicating that the MSS powders have not only nearly identical crystallinity, but also slightly better crystallinity than the high-temperature SSR powder samples after sintering.

To investigate the role of local compositional variations on ionic conductivity, sintered garnet electrolytes were fractured and examined via SEM-EDS and BSE imaging (Figure 7, and Figure S8, Supporting Information; results summarized in Table S5, Supporting Information). Each sample shows variability in the amount of Ta and Zr within different grains or regions of the sintered ceramic, as seen by the variability in the Ta M/Zr L peak ratios in the EDS spectra. In several cases, contrast differences can be clearly seen in the BSE-SEM images, with brighter areas corresponding to regions with higher Ta content. Some of the images reveal noticeable contrast differences between neighboring grains (see Figure 7e), but the contrast differences are generally not as stark as in the initial specimen where inhomogeneity was observed in our previous work.[40] This implies that while BSE imaging is useful to reveal significant compositional variability in a garnet electrolyte, the differences in composition between adjacent grains are best detected using localized chemical analysis such as EDS.
2.5. Correlations between Sample Processing Parameters and Ionic Conductivity

To better illustrate the effects of various parameters on the ionic conductivity of the different LLZTO samples, Figure 8 presents a summary of the aforementioned analyses investigating the role of synthesis temperature, Ta distribution in the sintered electrolyte, XRD peak broadening in the as-synthesized powder, and pellet density. While it is possible that some of the variation in ionic conductivity may arise from differences in the Li content (as sintering of Li garnets can be difficult to perfectly optimize), the sintering methods used here (specifically to supply excess Li2O by use of mother powder and Li2O2 in an enclosed sintering environment)\textsuperscript{[38]} are based on those shown\textsuperscript{[24]} to minimize or eliminate Li loss, and for these samples (with the exception of the PG-MSS sample), many pellets were sintered to approximately optimize sintering for each sample type, followed by selecting the sample with the highest ionic conductivity for further analysis. Figure 8a shows the total ionic conductivity of various LLZTO samples versus synthesis temperature, with no clear trend. Although the pellet density can generally be expected to have some effect on ionic conductivity, there is no strong overall trend for these samples with relative density either (Figure 8b), most likely because all of the samples possess good intergranular cohesion as evidenced by the predominately transgranular fracture\textsuperscript{[19,49]} shown in Figure 7. Our conclusion is that the reasonably high pellet density is a necessary but not sufficient condition to confer high ionic conductivity, which is especially clear when comparing the HB-MSS and 1×-SSR\textsubscript{1000} pellets, which display nearly identical relative density but a factor of two difference in conductivity. The degree of crystalline disorder in the as-synthesized powders also has no effect on ionic conductivity in the sintered pellets (Figure 8c).

However, trends emerge when examining the relationship between ionic conductivity and elemental inhomogeneity. The standard deviation of the Ta content in sintered pellets for various LLZTO samples is plotted in Figure 8d, showing an inverse correlation with the total ionic conductivity. LLZTO prepared by PG-MSS (indicated as a hollow circle) does not fit the general trend as well, which we attribute to the fewer number of pellets prepared and not fully optimized sintering conditions for this sample. However, the relatively low elemental inhomogeneity implies that using pyrochlores as reagents may be advantageous to minimize inhomogeneity, in addition to enabling lower synthesis temperature. When considering the effect of inhomogeneity on lattice conductivity (i.e., ignoring grain boundary impedance), the trend is even clearer (Figure 8e). Note the difference in ionic conductivity of the 1×-SSR\textsubscript{1000} samples sintered at 1100 versus 1200 °C; despite using the same powder, the two sintering temperatures result in different conductivities for optimized samples, which fits the trend of elemental inhomogeneity well. This may indicate that a shorter sintering operation at a higher temperature may reduce inhomogeneity more effectively than a longer sintering step at a slightly lower temperature. The strong correlation between lattice conductivity and inhomogeneity is particularly good evidence that local compositional variations have a deleterious effect on performance. This is consistent with the fact that the intrinsic Li-ion dynamics in garnet electrolytes are determined largely by the Li content\textsuperscript{[19]} (i.e., composition) and explain why the synthesis temperature or amount of crystalline disorder in the powders and even the relative density after sintering (so long as reasonably high density is achieved) have little effect on the performance of garnet solid electrolytes. In short, elemental inhomogeneity is the best explanation for the wide range of ionic conductivities in the various samples discussed herein.

Therefore, we attribute the main deleterious effect on ionic conductivity to the variability of Ta content in the sintered...
pellets as characterized by the magnitude of the standard deviation of Ta content between various individual crystalline grains in each specimen. We propose two main reasons for this effect. First, grains that possess insufficient Ta to fully stabilize the cubic phase will result in non-optimal Li-ion conduction, as the tetragonal phase is known\(^2\) to possess drastically lower ionic conductivity relative to the cubic phase (\(\approx 0.4 - 0.5\) mol Ta PFU needed at a minimum\(^4,8\)). In our case, we observed striations in fracture surfaces of some LLZTO pellets (Figure S9, Supporting Information, shows an HB-MSS pellet as an example), which were also observed by Thompson et al.\(^8\) and are associated with fracture of a tetragonal (or partially tetragonal) structured garnet ceramic. These striations corroborate the presence of partially tetragonal grains due to local lower Ta content. Although no obvious evidence of tetragonal LLZO can be observed in the XRD data in Figure 3 and Figure S1, Supporting Information, it is possible that a small amount is present but not discernable without neutron

Figure 7. BSE-SEM images and EDS spectra of different regions of sintered pellets from powders prepared by a) HB-MSS, b) mHB-MSS, c) PG-MSS, d) mixed-MSS, e) chloride-MSS, f) NAP, g) N-2×SSR\(_{950}\), and h) 1×SSR\(_{1000}\) sintered at 1200°C. Some of the BSE images had contrast and brightness enhanced to accentuate any differences in contrast between different regions of the image. Note that the darker contrast around grains in (d) for the mixed-MSS sample arises from the relatively higher porosity compared with other pellets. The SEM-EDS data for the 1×SSR\(_{1000}\) sample sintered at 1100°C for 12 h are shown in Figure S8, Supporting Information. Finally, some Al signal was observed (\(\approx 1.5\) keV for Al K X-ray signal) in the mixed-MSS, 2×SSR, and PG-MSS, the origin of which is unknown. In each case, Al signal is only observed in a single EDS spectrum.
diffraction as reported previously\cite{8}. Second, grains with too much Ta will have fewer free Li\(^+\) ions as charge carriers, also with the effect of reducing ionic conductivity\cite{9}. Furthermore, as the high ionic conductivity of superionic conductors such as Li garnets arises not from classical diffusion but rather from ensemble motion\cite{54}, it is sensible that maintaining uniformly optimal Li content (generally between 6 and 6.5 mol PFU\cite{1,9,23,55}) throughout the solid electrolyte is crucial to optimize ion conduction.

2.6. Discussion of Relationship between Thermodynamics and Kinetics of Formation on Elemental Inhomogeneity in Li Garnets

At this point, we have demonstrated that elemental inhomogeneity can occur in LLZTO nearly irrespective of the synthesis method and is often maintained even after sintering the powders at high temperatures to form densified ceramics. To understand this effect, insight into the thermodynamic stability of LLZTO is

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**Figure 8.** Comparison of the effect of various factors on room temperature total ionic conductivity in LLZTO powders studied herein, including a) the synthesis temperature used for synthesizing the specific garnet powder, b) the relative density of the pellet, c) the change in FWHM of Bragg reflections in the powder (as described previously), d) the standard deviation of Ta content residual in the sintered pellet describing elemental inhomogeneity, and e) effect of standard deviation of Ta content residual in the sintered pellet on lattice ionic conductivity in samples where it was measurable. The strongest effect observed is the inverse correlation between d) total ionic conductivity and e) particularly lattice ionic conductivity, whereas the other variables have no obvious correlation with ionic conductivity. Note that the PG-MSS sample is indicated as a hollow circle to denote the lack of extensive sintering optimization relative to other samples.
important. In the computational study of Miara et al., the LLZTO solid solution was shown to be increasingly energetically favorable (specifically, having a lower decomposition energy) for increasing Ta content. This implies a propensity toward forming Ta-rich garnets at some point during a reaction for the synthesis of LLZTO of a given composition. This energetic trend is supported anecdotally by our previous results showing that LLZTO forms at a slightly lower temperature than undoped, cubic phase LLZO (850 °C vs 900 °C, respectively, for 4 h synthesis time in the chloride-MSS medium).

Naturally, the minimum free energy condition of the entire ensemble of reagents can be expected to be that resulting from fully intermixed reagents, in this case the phase of nominal composition Li$_6$La$_3$Zr$_{1.4}$Ta$_{0.6}$O$_{12}$. However, the formation of other intermediate phases that substantially reduce the overall free energy of the system, especially those that are kinetically easy to form, can complicate the formation process of the target material. In fact, if the intermediates are only slightly less stable than the target material (or in the case of LLZTO grains with higher Ta content, more stable than the uniform nominal composition), the thermal energy required to push the entire ensemble of reagents to the thermodynamic energy minimum may be quite high. This has been demonstrated in other materials, such as Na$_{0.6}$MO$_2$ (M = Co and Mn) system. In this case, most of the net change in free energy of the reagents occurred during the formation of metastable intermediates, to the extent that considerably higher reaction temperatures were required to form the equilibrium phase despite its greater energetic favorability. As the thermodynamic driving force was low, the kinetics of formation were sluggish, implying that both the kinetics and thermodynamics of forming a given phase from an ensemble of reagents are critical to understand for developing an optimized synthetic approach. Furthermore, as metastable compounds such as LLZO and its doped analogues are generally considered to be entropically stabilized (with the entropy component of the free energy of a system dependent on the temperature), elemental inhomogeneity, if present, may be difficult to ameliorate with low synthesis temperatures. This need for a stronger thermal driving force to promote a sluggish reaction is the most likely explanation for the relatively good compositional uniformity of the LLZTO sample synthesized via SSR at 1000 °C (1×-SSR$_{1000}$).

Therefore, for a distribution of composition to occur during the formation of LLZTO, it is more likely that Ta-rich garnet phases form first and are maintained due to the locally lower free energy of that subset of reagents. Then, if conditions promoting solid-state diffusion are not maintained for sufficient time, or if the temperature is too low to facilitate solid-state diffusion after the garnet phase forms (as is more likely in the lower temperature MSS methods), the initial distribution of composition is retained even after the synthesis. In the case of SSR (schematically shown in Figure 9a), solid-state diffusion is slow and the effective cross-sectional area through which atomic species can diffuse is limited by the contact area between particles of reagents, which is why higher temperatures are required. In our SSR LLZTO materials, the use of multiple reaction steps with mixing in between or a higher single reaction temperature can substantially lessen the degree of elemental inhomogeneity. In the case of MSS (schematically shown in Figure 9b), dissolution of reagents also plays a role. As the molten salts act as a high-temperature solvent, reagents are more easily distributed during synthesis. For this reason, one would intuitively expect the compositional uniformity of MSS LLZTO to be better than that of SSR. While this is the case in some examples (especially comparing the HB-MSS and chloride-MSS powders to the 1×-SSR$_{1000}$ powders), the mechanisms of reagent dissolution and interdiffusion in the melt also bring some added complexity.

In MSS, there are generally two accepted reaction mechanisms for forming complex oxides: dissolution-precipitation and template-formation. In the former, all reagents have sufficient solubility in the chosen salt melt to readily dissolve, interdiffuse, and (in the ideal case) nucleate the desired phase from a uniform, homogeneous solution. In the latter, one or more reagents have limited or no solubility in the chosen melt, resulting in oxide formation by diffusion of the soluble reagents to the insoluble ones.

Figure 9. Depiction of evolution of reagents to form LLZTO in a) solid-state synthesis of LLZTO, showing effect of local compositional variation in reagents being preserved as the garnet phase is formed to produce a distribution of garnet crystals with variable composition, which requires excessive time at high temperatures to result in a uniform composition, and b) MSS of LLZTO where the higher relative solubility of Ta$_2$O$_5$ is hypothesized to result in an initial surplus of dissolved Ta species and early formation of Ta-rich garnet crystals, followed by slower dissolution of Zr species and late formation of Zr-rich garnet crystals.
and interfacial reaction on the surface of the insoluble reagent. Practically speaking, a mixture of both mechanisms is likely to occur, with one mechanism being favored over the other based on the relative solubilities of all reagents involved. In the case of LLZTO, the reasonably good solubility of La₂O₃ and Ta₂O₅ in molten salts and the comparably lower solubility of ZrO₂ along with the greater energetic favorability of LLZTO with higher Ta content, can be expected to act in concert to produce a distribution of garnet particles within the LLZTO solid solution. We hypothesize that this begins with the formation of the more energetically favorable, higher Ta-content garnet particles earlier in the reaction followed by higher Zr-content particles later due to these different solubilities. In fact, we suspect that the formation of higher Ta-content particles early in a MSS reaction allows more time for particle coarsening, which explains why the apparent mean composition of the mHB-MSS powder (Figure 2j) contains less than 0.6 mol of Ta PFU. In other words, the smallest particles (likely to be overrepresented on the TEM grid and, hence, EDS analysis) will tend to be the ones that formed later in the reaction (less energetically favorable), which, in turn, can be expected to be richer in Zr.

2.7. Discussion of Methods to Minimize Deleterious Elemental Inhomogeneity in Li Garnets

Based on the results presented in Figure 8d,e, it is clear that elemental inhomogeneity remaining after sintering of Ta-doped LLZO electrolytes has a negative effect on ionic conductivity and reduces intrinsic lattice ionic conductivity and not just total ionic conductivity. Therefore, rather than treating a garnet solid electrolyte as a uniform ionic conductor, a sintered, polycrystalline garnet solid electrolyte may be viewed as an ensemble of crystalline grains presenting individual resistor/capacitor elements both in parallel and in series with potentially different impedances. Grains with Ta content deviating too far from the optimal value will have increased impedance, causing Li⁺ to preferentially flow through adjacent grains with lower impedance. If too many of these grains exist in a sintered garnet electrolyte, they will block too many of the lower impedance pathways, leading to a bottleneck effect. This concept is graphically shown in Figure 10a. In such a situation, even a garnet electrolyte with high density, good grain cohesion, low grain boundary impedance, and the correct average composition will not possess the expected high ionic conductivity, because the proportion of low impedance pathways is too low.

Given the ubiquity of local deviations from the target composition in the samples investigated herein, approaches to mitigate it are crucial. The ideal case is to ensure a uniform composition during synthesis (Figure 10b), so that the sintering step can be optimized simply to minimize porosity and Li loss. One way to do this is with a brute force approach such as repeated SSR at high synthesis temperatures (see Table S1, Supporting Information, Wang and Lai, Huang et al., and Tsai et al.). In the results presented here, utilizing nanosized (i.e., pre-ball-milled) reagents (N-1×SSR and N-2×SSR) compared with bulk...
reagents (B-1 × SSR and B-2 × SSR) results in reduced inhomogeneity after two calcinations, as does using two calcination steps generally (2 × SSR over 1 × SSR). On the other hand, our 1 × SSR, sample shows comparable ionic conductivity to samples prepared with the aforementioned methods, implying that a single reaction at a higher temperature may be an attractive strategy to minimize the number of synthesis steps. Another option is single crystal growth from an appropriate melt (see Table S1, Supporting Information, Kataoka and Akimoto[34,35]). While the energy cost of each of these approaches is quite high, they can produce garnet electrolytes with very high ionic conductivity.

A different approach could be to use high sintering temperatures and long sintering times to allow sufficient solid-state diffusion to homogenize the composition of the electrolyte. Based on Fick’s second Law,[63] the time needed for a given species to diffuse is proportional to the square of the distance. Hence, as the distance needed to allow full interdiffusion of Zr and Ta increases (based on the particle size of the powder used), the time will increase quadratically. This view is shown in Figure 10c, where if particle sizes are large, conventional sintering times may not be long enough to enable solid-state diffusion to produce a uniform composition after densification. However, as Li garnets have a strong propensity toward Li_2O loss at the high temperatures necessary for sintering,[24,55] such long sintering strategies require a large amount of sacrificial garnet powder,[24,56,65] to continuously provide a high enough Li_2O vapor pressure[24] to allow good densification and maintain a high Li content[56] in the sintered electrolyte. This makes extended sintering time as a strategy to mitigate elemental inhomogeneity extremely cost prohibitive.

An alternative approach to minimize elemental inhomogeneity is to ensure that the diffusion lengths between garnet particles during sintering are minimized. A clear illustration of this approach is comparison of the HB-MSS and mHB-MSS LLZTO powders we reported previously.[40] In the HB-MSS method, elemental inhomogeneity present initially in the powder (Figure 2a) was observed even after sintering at 1300 °C, a temperature notably higher than is generally used for sintering garnet solid electrolytes. However, while the mHB-MSS powder has an even greater variation in the Ta content than the HB-MSS powder (Figure 2j, and Table S5, Supporting Information), this inhomogeneity is not preserved to as large of an extent in the sintered ceramic (Figure 8, and Table S5, Supporting Information). The reason for this apparent contradiction seems to be the markedly smaller particle size distribution of the mHB-MSS powder, with the majority of particles being <1 μm and less agglomerated than the HB-MSS powder.[40] This smaller particle size distribution allows solid-state diffusion to occur in a shorter amount of time during sintering, resulting in reduced inhomogeneity in the final garnet ceramic ( schematically shown in Figure 10d).

In the ideal case, the synthesis method chosen to produce garnet powders should be optimized, such that no elemental inhomogeneity occurs in the first place. However, this may be difficult to achieve as it will depend on the thermodynamics and kinetics of the various species as well as choice of dopants, synthesis temperature, etc. as discussed previously. As Ta-rich garnets are more energetically stable than Zr-rich garnets,[94] the driving force for interdiffusion of Ta out of the Ta-rich grains may also be locally reduced depending on the difference in composition between neighboring grains. The combination of a quadratic relationship between grain size and the time needed for interdiffusion, and the energetic favorability of Ta-rich grains can further explain the propensity for Ta-rich grains to be preserved even after sintering unless diffusion lengths can be reduced through processing. This result motivates the use of submicrometer to nanosized garnet powders. Our NAP combustion method is an example of minimizing diffusion distances during synthesis, as the pre-garnet particles that form even before all of the organic species are removed via combustion show relatively uniform elemental distribution, with minor inhomogeneity existing only on small length scales (i.e., ~100 nm).[38] For LLZTO prepared by NAP, reasonable uniformity can, therefore, be expected in the nanopowder despite the low synthesis temperature of 700 °C. Other methods, such as the co-precipitation/ co-decomposition type approaches[9] or sol–gel-type methods, due to initial molecular mixing of individual atomic species[22,66] may also be effective for this reason.

We suspect, however, that the situation shown in Figure 10c is quite common. For one thing, most SSRs are performed at as low a temperature of as possible while still forming the garnet phase, generally around 900 °C.[20,21,23,27,28] Some methods from the literature use multiple calcination steps with grinding between reactions,[13,21,24,26,34] but this is not always the case. Based on our observation of elemental inhomogeneity in the various materials presented here, we believe that variation in composition most likely also occurs in LLZTO prepared in other examples in the literature but has gone unnoticed. We, therefore, speculate that some of the variation in maximum ionic conductivity in the literature may be related to elemental inhomogeneity. Furthermore, we suspect that the optimum doping level is also related to the degree of inhomogeneity—if a synthesis method produces garnet powder with a narrow distribution in composition, the optimal doping level determined for that investigation should be closer to the intrinsic optimal doping level for LLZTO, whereas garnet powder with a wider distribution in composition will have a perceived optimum that minimizes the number of subcritically doped grains. This is because higher Ta content garnet (e.g., Li_6La_3ZrTaO_12) can still provide an ionic conductivity up to 0.24 mS cm^{-1}[67] whereas tetragonal LLZO has much lower conductivity.[2]

Though this study solely focuses on Ta-doped LLZO of a specific nominal composition, there is evidence that other garnet compositions are prone to similar challenges. For example, Hubaud et al. observed similar inhomogeneity in Al-doped LLZO with high resolution synchrotron XRD and 27Al nuclear magnetic resonance (NMR) spectroscopy wherein the as-prepared sample was an ensemble of garnets of slightly different Al content due to the difficulty in incorporating Al into the lattice.[68] In contrast, Posch et al. observed that the Li-hopping dynamics were quite uniform in a single crystal of Al-doped LLZO on account of the uniform composition; polycrystalline samples of similar composition displayed a broad range of Li-jump frequencies, which was attributed to a range of Li content due to inhomogeneous distribution of Al between particles.[69] It was also speculated[69] that regions of a polycrystalline garnet with insufficient Al doping would hinder long-distance Li-ion motion, a similar conclusion we make herein with Ta-doped...
LLZO. Smetaczek et al. utilized laser ablation inductively coupled plasma optical emission spectroscopy (LA-ICP-OES) to determine the variation in local composition across a sintered Al-doped LLZO electrolyte in conjunction with microcontact electrochemical impedance spectroscopy (EIS) to demonstrate that the local composition and impedance vary considerably across a single garnet membrane.[70] Badami et al. also observed a mix of related garnet phases due to Al contamination in sintered LLZTO electrolytes.[42] These observations and the results presented here indicate that the relative phase stability of doped garnets and intermediates depend on the dopant type and additives, implying that the formation of a distribution of garnets of variable composition is likely a common feature of LLZO synthesis in general, not just Ta-doped LLZO. Indeed, the choice of cationic dopants has a marked effect on the defect energy of LLZO, implying that the thermodynamics of LLZO depend on the dopant type.[71] Regardless of dopant choice or synthetic method, this work demonstrates the importance of understanding the local compositional homogeneity of a garnet solid electrolyte and provides perspective and a strategy to address elemental inhomogeneity. We hope that these results will provide tools to help other researchers improve the reproducibility and performance of garnet-type solid electrolytes in the important goal of enabling solid-state lithium batteries.

3. Conclusion

In this work, we have explored synthesis-related effects on the ionic conductivity of lithium-conducting garnets. Using XRD and PDF analysis for structural characterization, and chemical characterization via electron microscopy with energy dispersive X-ray spectroscopy, the effects of different synthesis mechanisms and synthesis temperatures in MSS, NAP combustion synthesis, and SSR are explored. In general, the lower temperature (i.e., 400–700 °C) synthesis methods produce Li-garnet powders with lower crystallinity as evidenced by peak broadening in XRD and PDF analysis, but not necessarily reduced ionic conductivity when consolidated into a dense electrolyte, because the crystallinity is improved during sintering. On the other hand, elemental inhomogeneity, comprising deviation in composition on a particle-by-particle basis, arises irrespective of the synthesis method and is often preserved in garnet electrolytes even after high-temperature sintering. This inhomogeneity arises initially during synthesis most likely due to a mixture of thermodynamic and kinetic factors unique to each synthesis method and can be significant even in conventional, high-temperature solid-state reactions. Although SSR is not always effective to ensure perfect uniformity of composition, using nanosized oxide precursors, repeated calcinations with intermediate ball milling, or higher synthesis temperatures are all strategies to increase the compositional homogeneity of the resultant LLZO powder.

The influence of synthesis temperature and relative density on the ionic conductivity of garnet electrolytes is not significant, but there is a noticeable inverse correlation between ionic conductivity and the degree of elemental inhomogeneity remaining in sintered electrolyte ceramics, especially when considering lattice ionic conductivity over total ionic conductivity. We attribute this effect to non-optimal Li content, as the amount of the Ta dopant varies on a grain-by-grain basis in sintered LLZO. However, high ionic conductivity is possible using each of the synthesis methods so long as the inhomogeneity can be eliminated at some point in the overall synthesis and processing scheme, showing that good performance can be achieved in garnet electrolytes formed from garnet powders obtained at very low synthesis temperatures (e.g., 550 °C). This exploration reveals that elemental inhomogeneity is another variable that negatively affects performance in Li garnets and is difficult to observe with routine characterization methods. We hope that this work serves as a guide for assessing the extent to which inhomogeneity may be present as well as provides methods to mitigate it and consistently enable high ionic conductivity in garnet-based solid-state batteries.

4. Experimental Section

Tantalum-doped LLZO (LLZTO) with the nominal composition Li$_x$La$_{4-x}$Zr$_{1-x}$Ta$_x$O$_{12}$ was synthesized by the SSR method from Li$_2$CO$_3$, La(OH)$_3$, ZrO$_2$, and Ta$_2$O$_5$ as described in the Supporting Information. In brief, two approaches were used for SSR LLZTO: first, a single calcination step at 1000 °C for 8 h was used (called “1×-SSR950”). Second, a two-step reaction with two calcination steps at 950 °C for 8 h each (with intermitent ball milling between calcinations) was used (called “1×-SSR950” for just the first step and “2×-SSR950” for the full two-step reaction). A slightly lower reaction temperature was used in the second case to reduce Li$_2$O evaporation. Furthermore, two sets each of 1×-SSR950 and 2×-SSR950 were prepared, one using bulk Ta$_2$O$_5$ and ZrO$_2$ and the other using pre-ball-milled Ta$_2$O$_5$ and nanosized ZrO$_2$, prefixed with “B” to denote bulk precursors (e.g., B-1×-SSR950) and “N” for nanosized precursors (e.g., N-1×-SSR950) as described in the Supporting Information.

Dense LLZTO pellets were obtained via conventional uniaxial pressing followed by pressureless sintering in air between 1100 and 1200 °C depending on the sample using the same approach reported in our previous works.[38,40,41] Details of the sintering conditions are found in Table S1, Supporting Information. Total room temperature ionic conductivity values of pellets with either graphite electrodes[34] or 20 wt% (1.3 mol%) Sn–Li electrodes[37] were determined based on fitting data from EIS and the sample geometry, as in our previous[34,37] work. The activation energy of Li-ion conduction was likewise measured as in our previous[38,40,41] works. The relative density of the in the Supporting Information. The sintered pellets were determined from the mass and sample geometry and compared with the theoretical value for Li$_x$La$_{4-x}$Zr$_{1-x}$Ta$_x$O$_{12}$ of n=5.5 g cm$^{-3}$.[64]

In addition to LLZTO from the SSR method, LLZTO samples of the same nominal composition obtained from MSS,[100] PG-MSS,[41] and NAP combustion[38] synthesis in our previous works were characterized by the aforementioned characterization techniques for comparison. No new samples were synthesized by these methods for the analysis conducted herein, so we refer the reader to our previous works for complete descriptions of the synthesis methods used. For sintered LLZTO samples from MSS or NAP combustion, the relative density, ionic conductivity, and activation energy (where measured) for samples examined herein are reported from our previous[38,40,41] works rather than from new samples. In this case, the same samples for which ionic conductivity, activation energy (where measured), and relative density values were reported were further analyzed in this work as with their respective powders. Sintered pellet samples derived from the various LLZTO powder synthesis methods were chosen for further EDS analysis from many (generally at least ten) sintering experiments based on the highest ionic conductivity and density obtained, such that sintering could be considered approximately optimized and Li$_2$O loss mitigated. The exception to this is the PG-MSS sample, for which only a few sintering experiments were performed.

Characterization methods and analyses using XRD, synchrotron X-ray PDF[74–78] analysis, SEM, TEM, STEM, and EIS are outlined in detail in the Supporting Information. In addition, methods for approximating composition of powders and pellets using EDS are outlined in the Supporting Information. In brief, EDS spectra for various compositions of LLZTO were
simulated for appropriate sample geometries and electron beam accelerating voltages (10 or 15 kV for SEM, 200 kV for STEM, and 200 or 300 kV for TEM) using the NIST DTSA-II software package and used to develop a regression based on the Ta M/Zr L X-ray peak ratio. Then, this regression was applied to the experimental EDS data. This approach was chosen in lieu of generating precise standards for each composition amenable to analysis on each of the various instruments used herein or utilizing common standardless analysis. While not aiming to be a true quantitative analysis, this approach rather is intended to allow robust qualitative comparison between the various samples analyzed in this work.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that supports the findings of this study are available in the supplementary material of this article. The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

garnet, Li7La3Zr2O12, lithium-ion conductors, sintering, solid electrolytes, solid solution

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