Lithium Garnet Li$_7$La$_3$Zr$_2$O$_{12}$ Electrolyte for All-Solid-State Batteries: Closing the Gap between Bulk and Thin Film Li-Ion Conductivities

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The high ionic conductivity and wide electrochemical stability of the lithium garnet Li$_7$La$_3$Zr$_2$O$_{12}$ (LLZO) make it a viable solid electrolyte for all-solid-state lithium batteries with superior capacity and power densities. Contrary to common ceramic processing routes of bulk pellets, thin film solid electrolytes could enable large-area fabrication, and increase energy and power densities by reducing the bulkiness, weight and critically, the area-specific resistance of the electrolyte. Fabrication of LLZO films has nonetheless been challenging because of lithium losses and formation of impurity phases that result in low densities and poor ionic conductivities as compared to bulk pellets. Here, a scalable method for fabricating submicron films of LLZO employing co-sputtering from doped LLZO and Li$_2$O targets is presented. A record ionic conductivity of 1.9 × 10$^{-4}$ S cm$^{-1}$ is measured for dense and uniform cubic-phase Ga-substituted LLZO films annealed at 700 °C in oxygen, which is comparable to the values in high-temperature sintered pellets and outperforms by one order of magnitude the latest record for LLZO thin films as well as the typical conductivities in the well-established LiPON electrolyte. This result is an important milestone to realize all-vacuum deposited solid-state batteries with higher power density.

1. Introduction

Solid-state fast lithium-ion conductors have been gathering increasing attention in recent years as a feasible alternative to traditional liquid electrolytes in Li-ion batteries (LIBs). The concept of an all-solid-state LIB has the potential to overcome the physicochemical limits of the standard liquid-based LIBs in terms of energy and power densities and rate capability, and is intrinsically safer.[1] Enabling the use of metallic lithium as anode material is a key aspect for reaching the predicted high energy densities.[2] Even though a wide variety of materials with high ionic conductivities have been evaluated (e.g., LGPS, LPS, and LATP), the range of possibilities becomes narrower when also sieving for electrochemical stability against metallic lithium and high potential cathode materials. Lithium garnet Li$_7$La$_3$Zr$_2$O$_{12}$ (LLZO) has demonstrated not only a high ionic conductivity (in the range of 0.1 to 1 mS cm$^{-1}$) but also a wide electrochemical stability window (from 0 to ≈6 V vs Li/Li$^+$), which makes it a promising electrolyte candidate for the development of all-solid-state LIBs.[3]

LLZO can appear in different crystalline polymorphs. At room temperature, pure LLZO has only one thermodynamically stable phase, the tetragonal phase (space group I4$_1$/amd), which has a limited ionic conductivity of about 10$^{-6}$ S cm$^{-1}$. At high temperatures (from 150 up to 650 °C, depending on the preparation method and initial stoichiometry of the precursors),[4,5] LLZO undergoes a phase transformation into the high-temperature cubic phase (space group Ia$3d$), with superior ionic conductivity.[6-8] The difference in ionic conductivity arises from the different ion transport mechanisms characteristic of each phase. In the cubic phase, which presents a large amount of Li sites vacancies, ions hop from site to site asynchronously following well-defined pathways. This mechanism requires a significantly lower activation energy than the collective ionic movement that takes place in the tetragonal phase.[9]

The high-temperature cubic phase can be stabilized at room temperature by adding aliovalent dopants. Al$^{3+}$ and Ga$^{3+}$ are the most commonly employed dopants in the synthesis of cubic LLZO.[7,10-12] The aliovalent cation substitutes the Li sites creating therefore additional vacancies. Besides the stabilization of the cubic phase, the dopants play also a role in other properties of the electrolyte, such as the density and the critical current density. Our group previously reported the effect of aluminum in the density of LLZO films.[13] Pesci et al. reported...
a link between the dopant and the critical current density in the electrolyte.\cite{14}

LLZO is generally investigated in the form of pellets, which are fabricated following ceramic sintering processes that require long processing times (above 10 h) and high temperatures (about 1200 °C). This process results in pellets with a diameter of a couple centimeters at maximum and thickness in the millimeter range. Typically these pellets are polished to obtain a smooth surface and remove degradation residues, resulting in significant waste of raw material. This form factor and processing approach is a major drawback for the development of solid-state batteries with a lithium garnet electrolyte. From an industry perspective it is necessary to investigate alternative fabrication methods that enable larger-scale and faster production at lower costs.

Thin-film processing of lithium garnet electrolytes has recently gained attention as an alternative fabrication method.\cite{15} This approach allows to lower the manufacturing temperature by more than 400 °C as well as reduce the thickness of the electrolyte material by more than three orders of magnitude (from hundreds of micrometers to a few hundred nanometers). However, to date all the submicrometer thin films reported in literature exhibit ionic conductivities at least one order of magnitude below the typical bulk values. So far the highest ionic conductivity (2.9 × 10^{-5} S cm^{-1}) for submicron LLZO films was achieved by Pfenninger et al. using a pulsed-laser deposition (PLD) process.\cite{16} Still, this is not enough to match the resistances of state-of-the-art liquid electrolytes. According to estimations by Samson et al., submicron films with an ionic conductivity above 0.1 mS cm^{-1} are necessary to be on a par with standard liquid electrolytes. Yi et al. have been able to measure conductivities above 0.1 mS cm^{-1} but in sheets in the micrometer range and only after annealing at 1130 °C.\cite{17} Typical challenges in the thin film processing are the high amount of lithium losses occurring during annealing (due to the high surface to volume ratio) and the consequent necessity to employ lower temperatures, which has a negative impact on the density and crystallinity of the LLZO films. Ultimately, these processing limitations have a detrimental effect on the ionic conductivity of the films.

In this work we present a scalable method to fabricate submicron LLZO films by co-sputtering doped LLZO and Li2O, and subsequent annealing at temperatures between 600 and 700 °C. By controlling the excess of Li in the films and choosing the appropriate dopant, ionic conductivities and densities comparable to the bulk are achieved. This study demonstrates for the first time that it is possible to obtain ionic conductivities above 0.1 mS cm^{-1} in lithium garnet submicron films, making it possible to match the resistances of standard liquid electrolytes.

2. Results and Discussion

2.1. Fabrication of Submicron LLZO Films: Overlithiation and Doping

LLZO films were prepared by co-sputtering stoichiometric LLZO and Li2O, as schematically shown in Figure 1a. The deposition was carried out at room temperature and later the films were annealed for 1 h in pure oxygen at atmospheric pressure. Li2O is added to the as-deposited films to compensate the lithium losses occurring during the sputtering processes and specially during the annealing step after deposition. As previously reported by our group, the amount of lithium excess has to be finely tuned in order to obtain dense and phase pure films.\cite{16} If the amount of Li2O is too low, lithium-deficient phases (namely La2Zr2O7) are formed and if the excess of lithium is too high, pores appear in the film due to the evaporation of excess lithium oxide during annealing. The overlithiation can be tuned by adjusting the sputtering rates of the LLZO and Li2O targets, simplifying the multilayer deposition approaches previously reported to compensate lithium losses.\cite{16} An optimal value of 4.0(5) mols of extra lithium per formula unit (p.f.u.) of LLZO was employed.

Dopants play an essential role in the crystallization of the ionic-conductive cubic LLZO phase and also can assist in the sintering of the films. In our work we investigated films with two common dopants, aluminum and gallium, and compared them to non-doped LLZO films. To incorporate the dopant in the film, doped LLZO targets (with approximate stoichiometries of Li_{k,23}Al_{0,23}La_{0,7}Zr_{0,12}O_{12} and Li_{k,23}Ga_{0,23}La_{0,7}Zr_{0,12}, see Table S1, Supporting Information, for ICP-MS measurements of the targets) were employed. This approach simplifies the deposition process and guarantees a higher homogeneity of the dopant distribution in the film, as compared to the multilayer deposition approaches previously reported by our group.\cite{13,18}
Films were prepared on MgO single-crystal substrates, which present a low reactivity and diffusivity at the processing temperatures employed and therefore allow studying the properties of the films without interferences from the substrate. This type of substrate has been commonly used in the investigation of lithium garnet electrolyte thin films.[16,18–23] Figure 1b shows a picture of the annealed LLZO on a MgO single crystal substrate. As one can observe, the films are mostly transparent in the visible spectrum and have a shiny surface that reflects slightly greenish light.

### 2.2. Chemical Composition

Table 1 shows the stoichiometry of the non-doped and doped LLZO films after annealing at 700 °C, determined by Rutherford back-scattering spectrometry (RBS) and elastic recoil detection analysis (ERDA). The La signal was used for normalization and assumed to be 3. In all cases the Zr/La ratio matches well the expected theoretical 2/3 ratio. The lower amount of Li present in the Al- and Ga-doped films relative to the non-doped film is expected from the lower Li content in the doped targets (see Table S1, Supporting Information), which at the same time is a consequence of the trivalent dopant playing a role as a Li substitute. The Li content is slightly substoichiometric in all three samples. This lithium deficiency can be partially a result of the massive lithium loss occurring during the annealing step. However, it must also be noted that the samples had to be shortly exposed to air prior to the measurement, which leads to the formation of some LiOH and Li2CO3 on the surface and therefore the loss of lithium from the film. The amount of Al and Ga is slightly higher than what would be expected given the target compositions but it is known that the protonation of the film that occurs during the XRD measurement, as the sample is exposed to air and a reaction of the film with moisture and CO2 takes place.[25] It is known that the protonation of LLZO leads to a phase transition from tetragonal to cubic phase, which explains the convergence of the lattice constants.[13] The parameters of the doped cubic LLZO films are slightly smaller than previously reported values measured in LLZO powders and single crystals.[24,26]

**Table 1. Stoichiometry of the crystalline LLZO films determined by RBS and ERDA (La signal used for normalization).**

|          | Li    | Zr    | O     | Al     | Ga     |
|----------|-------|-------|-------|--------|--------|
| LLZO     | 6.1(6) | 2.05(15) | 12.5(15) | –      | –      |
| Al-LLZO  | 5.9(6) | 2.15(15) | 13.0(15) | 0.35(5) | –      |
| Ga-LLZO  | 5.1(5) | 2.25(15) | 13.0(15) | –      | 0.32(3) |

Uncertainty noted in parentheses.

### 2.3. Crystalline Phase

The crystallinity of the crystallized films was evaluated by grazing-incidence X-ray diffractometry (GI-XRD). Figure 2 shows the XRD patterns of non-doped, Al-doped, and Ga-doped LLZO films annealed at 700 °C. In all three cases a predominant LLZO phase is observed, but with differences in the lattice parameters. To identify the phase and determine the lattice constants, Rietveld refinements of the XRD patterns were performed (see Figure S1, Supporting Information, for more details). The following reference structures were respectively employed: tetragonal LLZO with the space group I41/acd (ICSD 246817),[6] cubic Al-doped LLZO with the space group Ia3d (ICSD 185539),[7] and cubic Ga-doped LLZO with the space group I43d (ICSD 430603).[24]

**Figure 2. Grazing-incidence X-ray diffraction patterns of the non-doped, Al-doped, and Ga-doped LLZO films annealed at 700 °C after deposition.**

In red the Rietveld refinements of the patterns employing as reference the following phases respectively: tetragonal LLZO with the space group I41/acd (ICSD 246817),[6] cubic Al-doped LLZO with the space group Ia3d (ICSD 185539),[7] and cubic Ga-doped LLZO with the space group I43d (ICSD 430603).[24] The refined lattice constants are presented in Table 2.

In the case of non-doped LLZO, the difference between lattice constants a and c is lower than what is expected from a pure tetragonal LLZO phase.[6] This can be explained by the protonation of the film that occurs during the XRD measurement, as the sample is exposed to air and a reaction of the film with moisture and CO2 takes place.[25] It is known that the protonation of LLZO leads to a phase transition from tetragonal to cubic phase, which explains the convergence of the lattice constants.[13] The parameters of the doped cubic LLZO films are slightly smaller than previously reported values measured in LLZO powders and single crystals.[24,26]

Besides the predominant LLZO peaks, some small impurity phases can be detected. One likely impurity is Li2CO3, with main peaks at 21.4° and 31.8°, which is expected to appear as a result of the air-induced degradation. Li2ZrO3 could be responsible for the small peak at 20.3°. In the case of the Ga-doped LLZO film, the peaks at 21.5°, 22.5°, and 35.9° can be assigned to LiGaO4.[18] In the Al-doped LLZO film, the small peak at 28.4° could be assigned to the pyrochlore La2Zr2O7 phase.

**Table 2. Lattice constants obtained from the Rietveld refinements of the LLZO films’ XRD patterns.**

|          | Space group | a [Å]       | c [Å]       |
|----------|-------------|-------------|-------------|
| LLZO     | I41/acd     | 13.0254(59) | 12.8900(61) |
| Al-LLZO  | Ia3d        | 12.9490(36) | –           |
| Ga-LLZO  | I43d        | 12.9515(37) | –           |
2.4. Morphology and Elemental Distribution

The morphology of the films was investigated by imaging their surface and cross section with a scanning electron microscope (SEM). Figure 3 shows the images of the non-doped and doped films annealed after deposition. The thicknesses of the films are in the range 450 to 550 nm. In all three cases a dense and conformal film is observed, with no sign of cracks and pin-holes. Some porosity and surface roughness is observed in the non-doped LLZO films, evidencing the role of the dopants in the microstructure of the films. The Ga-substituted film also shows some internal porosity but in comparison to the non-doped film, presents a significantly smoother surface. The density and compactness of the Al-doped film is especially high, as expected from the effect of Al as a sintering aid.[13,14] In the non-doped film, a surface layer of Li₂CO₃ can be observed. This results from the exposure of the films to air during the preparation of the cross sections. This superficial Li₂CO₃ layer does not appear so evidently in the doped films. The dopants play indeed a role in mitigating the degradation of LLZO in the presence of CO₂ and moisture, likely by forming an oxide passivation layer on the surfaces that hinders the proton-lithium exchange mechanism.[31]

The films were further investigated by characterizing the elemental distribution both across the cross section and on the lateral plane. We employed a Ga focused ion beam (FIB) coupled to a time-of-flight secondary ion mass spectrometer (ToF-SIMS). This technique allows for detection of all elements (light and heavy) with nanoscale resolution and very high sensitivity. Other techniques with similar resolutions like STEM/EDX cannot be used for light elements like Li.[29] However, ToF-SIMS is in general not a quantitative method because the “matrix effects” (the interactions between the analyte and the surroundings) influence the ionization yield by several orders of magnitude.[30] Figure 4 shows the depth profiles of the matrix elements (²⁷Li⁺, ¹³⁹La⁺ and ⁹⁰Zr⁺), dopant (²⁷Al⁺), and substrate material (²⁴Mg⁺). The elemental distribution maps over a lateral area of 10 × 10 μm² at different depths are also presented, together with their corresponding secondary electron image collected in situ during the sputtering process at each depth. To avoid edge effects, only the central 5 × 5 μm² was considered for generating depth profiles. Figure S2, Supporting Information, shows SEM images of the film surfaces before and after the FIB-TOF-SIMS measurement, in which a uniformly sputtered crater can be observed.

In all three cases well-correlated and homogeneous distributions of the ¹³⁹La⁺ and ⁹⁰Zr⁺ signals are observed across the thickness of the film. The inhomogeneities present in the lateral plane in the non-doped LLZO film (Figure 4a) are due to the presence of pores in the film and roughness on the surface (i.e., topology effects). Contrarily, in all three films the ⁷Li⁺ signal seems to be slightly lower on the upper part of the film (after the first surge that corresponds to the sample’s surface). This tendency is more noticeable in the non-doped and Ga-doped films. The evaporation of lithium during the annealing step can be the reason for this gradient. The incorporation of Al mitigates the segregation of Li towards the surface by forming a lithium aluminate passivation layer at the grain boundaries,[13,14] hence the less graded ⁷Li⁺ signal in the Al-doped film. On the surface, the ⁷Li⁺ signal is significantly higher, likely due to the presence of lithium hydroxide as a result of exposure to air while loading the samples into the measurement system.[31,32]

Regarding the distribution of the dopant, only Al could be investigated due to the use of a Ga ion beam for sputtering. In the
Al-doped LLZO film, the $^{27}$Al$^+$ signal appears homogeneously distributed in the film, both in depth and over the lateral plane. This result differs greatly from the observed segregation of Al in films prepared by multilayer deposition of LLZO and Al metal that our group previously reported,$[^{13}]$ as well as in pellets,$[^{14,28,33}]$. This result implies that the processing method here employed guarantees a better distribution of the Al through the film. The crystalline phase also evidences this improved distribution of the dopant. In our previous work the Al-doped LLZO films had a mixed cubic/tetragonal phase whereas in this work the Al-doped films crystallize only in the cubic phase. In the non-doped and Ga-doped LLZO films, the $^{27}$Al$^+$ signal is two orders of magnitude lower, evidencing that only trace amounts of Al are present in the film.

2.5. Ionic and Electronic Conductivity

The ionic conductivity of the films was investigated by employing impedance spectroscopy (IS). Gold contacts were thermally evaporated on the crystallized films with a spacing of 200 μm. The measurements were carried out in an in-plane configuration, as shown in Figure 5a. Due to the high reactivity of the precursor compounds and the high processing temperatures, the use of a metallic back contact is unfeasible as non-conductive phases are formed at the interface. Several experiments with different back contacts (Pt, Au, Ta, TiN, Ni-Al-Cr$[^{34}]$) were carried out resulting in all cases in highly resistive interfaces. We employed therefore the above-mentioned in-plane architecture, which is widely used to characterize conductivities in thin films.$[^{35}]$ The high electrode separation to film thickness ratio guarantees a low measurement error due to surface and fringe conductance.

Figure 5b shows the Nyquist plots of the complex IS measurements at room temperature for the three types of LLZO film investigated (non-doped, Al-doped, and Ga-doped). A significant difference in resistances is observed between the doped LLZO films and the non-doped film, as expected from the difference in crystalline phase. The Nyquist plots reveal in
Figure 5. Electrical properties of the LLZO thin films. a) Picture and schematic of the measurement configuration. b) Nyquist plot of the complex impedance at room temperature of the non-doped, Al-doped, and Ga-doped LLZO films, with the respective equivalent circuit fitting. c) Equivalent circuit employed for the interpretation of the complex impedance measurements and extraction of the ionic conductivities. d) Comparison of the ionic conductivities measured in this work with the state-of-the-art values reported for LLZO pellets, sheets, and thin films, as a function of the processing temperature. References can be found in Table S3, Supporting Information. e) Arrhenius plot of the effective ionic conductivities at different temperatures. f) DC polarization curve over time, used to determine the electronic conductivity. g) Arrhenius plot of the electronic conductivities at different temperatures.
all three cases two conduction regimes, likely linked to the conduction through the bulk and through the grain boundaries. In the case of the non-doped and Al-doped films, both contributions can be well distinguished but in the Ga-doped film they are strongly overlapped.

To extract the resistance and capacitance parameters that control the ionic dynamics in the film, the complex impedance spectra were fitted with the equivalent circuit shown in Figure 5c. This equivalent circuit, proposed by Huggins to model ionic conductors,[36] accounts for the contact resistance ($R_{\text{contact}}$), the geometric capacitance ($C_{\text{geom}}$), bulk conductance ($G_b$), grain boundary conductance ($G_{\text{g.b.}}$), and charge polarization at the electrode-electrolyte interface ($C_{\text{PE}}$). The simulated complex impedance resulting from the fitting is plotted in Figure 5b. Figure S3, Supporting Information, shows the residuals of the fitting, indicating deviations below 2% for most of the frequency range fitted.

From the fitted bulk and grain boundary resistances, the ionic conductivities shown in Table 3 were calculated according to the following equation:

$$\sigma = \frac{l}{(R \cdot w \cdot t)}$$

where $R$ is the resistance, $l$ is the electrode separation, $w$ the electrode width, and $t$ the film thickness. The effective ionic conductivity accounts for both the bulk and grain boundary contributions. To verify the consistency of these values, the complex electric modulus was also fitted to extract the effective ionic conductivity (see Figure S4, Supporting Information). An explanation on this method can be found in the Supporting Information. The electric modulus analysis results in slightly higher but consistent values, as presented in Table S2, Supporting Information.

The bulk conductivities measured in the three types of LLZO thin films that we studied are comparable to the state-of-the-art values reported for high-temperature sintered pellets. Wolfenstein et al. investigated the densification of tetragonal LLZO pellets and measured ionic conductivities up to $1.2 \times 10^{-3}$ S cm$^{-1}$.[8] Rettenwander et al. studied the ionic conductivities in LLZO pellets doped with Al and Ga and reported bulk ionic conductivities of $2.6 \times 10^{-4}$ S cm$^{-1}$ for Li$_{0.4}$Al$_{0.6}$La$_{0.5}$Zr$_{0.5}$O$_{2.5}$ and $1.2 \times 10^{-5}$ S cm$^{-1}$ for Li$_{0.4}$Ga$_{0.6}$La$_{0.5}$Zr$_{0.5}$O$_{2.5}$, in good agreement with our results.[37] The difference in ionic conduction between Al- and Ga-doped LLZO has been recently investigated employing molecular dynamic simulations and attributed to different interaction strengths of the dopant with the neighboring Li$^+$ vacancies.[18]

When comparing to the state-of-the-art submicron LLZO thin films, the effective ionic conductivity of the here reported Ga-doped films outperforms by about one order of magnitude the record value of $2.9 \times 10^{-3}$ S cm$^{-1}$ reported by Pfenninger et al. in Al and Ta co-doped LLZO films deposited by PLD and post-annealed at 660 °C.[16] These new conductivity values also exceed by one order of magnitude the previous values reported by our group for sputtered Al-doped LLZO[33] and Ga-doped LLZO thin films,[38] which were prepared using a multilayer deposition approach. When comparing to the standard LiPON solid-state electrolyte, which is commonly used in commercial solid-state thin film batteries, the ionic conductivities of the LLZO films here reported outperform by two orders of magnitude the standard conductivities of this material.[19]

Figure 5d puts the ionic conductivities that we report in perspective with the most relevant reports on LLZO pellets (>200 μm), sheets (1–200 μm), and thin films (<1 μm). References to these values can be found in Table S3, Supporting Information. The ionic conductivities are plotted with respect to the annealing temperature at which the LLZO is processed, as this is a key factor for the eventual industrialization of this type of electrolyte. One can observe that the ionic conductivity of the Ga-doped LLZO films investigated in this work are comparable to the values reported for thick pellets but with a three orders of magnitude lower thickness and prepared at about 400 °C lower processing temperature. The significantly lower thickness and processing temperature can have a potential advantage in the industrial development of LLZO as a solid-state electrolyte.

To determine the activation energy of the ionic conductivity, IS measurements were performed at set temperatures ranging from 300 to 650 K. The actual temperature on the sample’s surface was measured during the IS measurement employing a temperature sensor (see picture in Figure 5a). Figure S5, Supporting Information, shows the modulus of the complex impedance at the different measurement temperatures, from which the effective ionic conductivities were extracted following the equivalent circuit fitting procedure previously described. Figure 5e shows the Arrhenius plot of the ionic conductivity of the three different samples. The data was fitted to the Arrhenius equation to obtain the activation energies ($E_a$) displayed on the plot.

The non-doped film shows an $E_a$ of 0.50(3) eV, which is higher than the theoretically predicted value 0.4 eV by Meier et al.[51] but is comparable to the values measured experimentally in bulk tetragonal LLZO.[40] In the case of the doped LLZO films, two different regimes appear. At lower temperatures there is a difference in $E_a$ of about 0.1 eV (0.38(1) eV in the Ga-LLZO film and 0.49(4) eV in the Al-LLZO film), a difference that is in good agreement with the results for sintered pellets of Rettenwander et al.[17] This difference disappears in the high-temperature regime (above 100 °C), in which the $E_a$ of both doped LLZO films converges to 0.32(3) eV. This non-Arrhenius behavior was previously observed in the Ga-doped films investigated by Rawlence et al.[28] Cuervo-Reyes et al. attributed this bending to ion-ion correlation effects at higher temperatures.[41] Further experiments would be required to confirm the physical mechanism responsible for this effect.

The $E_a$ at lower temperatures measured in the Al-doped LLZO film is comparable to the values previously reported in thin films (0.46 eV by Pfenninger et al.,[16] 0.47 eV by Lobe et al.,[32] and 0.48 eV in our previous work[15]) but lays far from

| $\sigma_{\text{bulk}}$ [S cm$^{-1}$] | $\sigma_{\text{g.b.}}$ [S cm$^{-1}$] | $\sigma_{\text{eff}}$ [S cm$^{-1}$] |
|---------------------------------|---------------------------------|-------------------------------|
| 9.11(55) $\times 10^{-4}$ | 5.53(33) $\times 10^{-4}$ | 3.44(21) $\times 10^{-4}$ |
| 1.32(13) $\times 10^{-4}$ | 8.22(82) $\times 10^{-5}$ | 5.06(51) $\times 10^{-5}$ |
| 1.78(4) $\times 10^{-3}$ | 2.14(4) $\times 10^{-4}$ | 1.91(4) $\times 10^{-4}$ |

Extracted from the equivalent circuit fitting of the complex impedance spectra.
the best values reported in pellets and sheets sintered at high temperatures (0.27 eV by El-Shinawi et al.\cite{43} and 0.35 eV by Yi et al.\cite{44}). Regarding the Ga-doped LLZO film, the $E_a$ of 0.38(1) eV in the lower-temperature regime and 0.32(3) eV in the higher-temperature regime constitute a significant improvement with respect to previously reported values in Ga-doped LLZO thin films (0.66 eV and 0.38 eV by Rawlence et al.\cite{18}). When comparing to the best high-temperature sintered Ga-doped LLZO pellets (0.25 eV by Wu et al.\cite{35}) and sheets (0.28 eV by Yi et al.\cite{17}) reported, this $E_a$ value is slightly higher.

The electronic conductivities of the different LLZO films were also measured. A DC polarization of 0.5 V was applied at the electrodes and the current evolution measured over 1 h. The polarization curves at room temperature are shown in Figure 5f. The steady-state current value can be attributed to electronic conduction, as the electrodes are ion blocking. The electronic conductivities are similar in the three type of films: 6.88(203) $\times 10^{-7}$ S cm$^{-1}$ in the non-doped LLZO, 1.77(14) $\times 10^{-7}$ S cm$^{-1}$ in the Al-doped LLZO, and 1.35(23) $\times 10^{-7}$ S cm$^{-1}$ in the Ga-doped LLZO film. These values agree well with previous investigations of the electronic conductivity in LLZO pellets.\cite{12,46} The temperature-dependent Arrhenius plot of the electronic conductivities is shown in Figure 5g. One can observe that the electronic conductivity increases with temperature, but with an activation energy lower than the one of the ionic conductivity. Han et al. recently reported that the high electronic conductivity in LLZO in comparison to other solid-state electrolytes (namely LiPON) could be linked to the formation of lithium dendrites in the electrolyte.\cite{46}

2.6. Processing Temperature and Ionic Conductivity

The compatibility of the electrolyte with electrode and current collector materials is highly dependent on the processing temperatures. Lowering the processing temperature is therefore essential for enabling industrial up-scaling of this technology. Uhlenbruck et al. reported that at temperatures above 700 °C LLZO and LiCoO$_2$ react and decompose forming an ion-blocking interface.\cite{37} This can be avoided by adding an interfacial coating, as reported by Kato et al. for pellets\cite{38} and our group for thin films,\cite{33} but at the expense of increased fabrication complexity.

The films previously presented in this work were processed at a temperature of 700 °C, which is significantly lower than any of the state-of-the-art sintering processes of LLZO pellets (generally above 1000 °C). Still this temperature could be too high for processing LLZO in combination with common cathode, current collector, and substrate materials. Therefore we attempted further lowering the annealing temperature and investigated its effect on the LLZO film’s crystallinity and ionic conductivity.

Ga-doped LLZO films were prepared in the conditions previously described and annealed at temperatures ranging from 500 to 800 °C. Figure 6a shows the GI-XRD patterns of the annealed films as well as the pattern of an as-deposited film. The as-deposited film presents an amorphous phase, as evidenced by the broad peak in the XRD pattern. From 500 to 700 °C we observe a transition from the amorphous phase to the cubic LLZO crystalline phase with well-defined Bragg peaks. The film annealed at 800 °C exhibits the lithium-deficient La$_2$Zr$_2$O$_7$ phase, that results from excessive lithium losses.

The ionic conductivity at room temperature and activation energy of the films annealed at different temperatures are displayed in Table 4 and their corresponding Arrhenius plots are shown in Figure 6b. The Li-ion conduction in the film annealed at 500 °C is strongly influenced by the low conductivity of the amorphous LLZO phase. Garbayo et al. reported that in LLZO thin films annealed at 500 °C a polymorphous phase dominates the films structure with some disconnected crystalline regions.\cite{49} The ionic conductivity values that they measured in their glassy LLZO films are in the same order of magnitude than the value we extrapolated from the Arrhenius plot of the film annealed at 500 °C. This conductivity value is also in the same range as that of amorphous as-deposited films. By increasing 100 °C, the conductivity jumps by four orders of magnitude. At 600 °C the film consists predominantly of the conductive crystalline LLZO phase, which results in a remarkably high ionic conductivity of about $10^{-3}$ S cm$^{-1}$. At 700 °C the crystallinity of the film further improves, resulting in the highest ionic conductivity. If the annealing temperature is further increased, the ionic conductivity rapidly degrades as a
result of an increased lithium loss and the formation of non-conductive secondary phases.

These results point out that it is possible to obtain conductive crystalline LLZO films at temperatures as low as 600 °C. This difference in 100 °C can be decisive for the combination of LLZO with cathode materials like LCO or NMC.[50] In a follow-up work we will demonstrate the use of this solid-state electrolyte in a thin-film solid-state battery architecture, employing LiCoO2 as cathode material and Li metal as anode. The lowering of the processing temperatures and the engineering of the interfaces are key factors to crystallize LLZO on top of a cathode material and obtain a low resistance interface.

3. Conclusions

Lithium garnet LLZO can enable the fabrication of solid-state batteries with increased energy density and rate capability, in comparison to the conventional liquid electrolyte Li-ion batteries. Its high ionic conductivity and electrochemical stability against metallic lithium and high potential cathode materials that have been reported for bulky pellets are indeed promising signs. However, to scale up this technology, methods to deposit films of this material on large areas and at lower processing temperatures are essential. Even though in bulk this material has proven to be an excellent solid-state electrolyte, to date the films and highly-conductive cubic phase, these dopants also assist in the densification of the films and improve the stability of the material in air.

The 500 nm-thick Ga-doped LLZO films presented in this work exhibit an ionic conductivity of 1.9 × 10^-4 S cm^-1, which outperforms by an order of magnitude the values previously reported in thin films and closes the gap with the standard values measured in thick LLZO pellets sintered at high temperatures. This value also outperforms by about two order of magnitude the typical conductivities reported for LiPON, an electrolyte material that is commonly employed in the development of thin film batteries. The thickness and ionic conductivity of the films here investigated allow to match the area-specific ionic resistances of conventional liquid electrolytes in a standard Li-ion battery configuration. These results constitute a milestone towards the development of LLZO-based solid-state batteries with higher power and energy densities.

4. Experimental Section

Thin Film Deposition: Overlithiated lithium garnet films were deposited at room temperature in a radio-frequency (RF) magnetron sputtering system (Orion, AJA International Inc.) with a confocal off-axis target configuration. Li7La3Zr2O12, Li6.25Al0.25La3Zr2O12, Li6.25Ga0.25La3Zr2O12, and Li2O targets from Toshima Manufacturing Co. were employed. The sputtering process was performed at 0.3 Pa using a 50 sccm Ar + 1 sccm Ar/O2 gas flow. The deposition rate of each target was controlled independently via the sputtering power and monitored using a quartz crystal microbalance (QCM) sensor. The films were deposited on 1 × 1 cm² (100)-oriented single-crystal MgO substrates (Jiangyin Maideli Advanced Materials Co., Ltd.).

The as-deposited LLZO films were annealed in a tube furnace (Carbolite GHA 12/300) at temperatures ranging from 500 to 800 °C for 1 h with a heating/cooling ramp of 2.5 °C min⁻¹. The annealing was carried out with an oxygen flow at atmospheric pressure. After annealing the samples were transferred without exposure to air to an argon-filled glovebox, to avoid the formation of Li2CO3 on the surface.

Characterization: The composition of the samples was characterized by Rutherford back-scattering spectrometry (RBS). Measurements were performed using a silicon charged particle detector under 168°. The collected RBS data were analyzed by the RUMP code.[53] The Li content was determined by elastic recoil detection analysis (ERDA) with a 13 MeV 127I⁺ primary beam and a combination of a time-of-flight spectrometer with a gas ionization detector. Data analysis was accomplished by custom software.

The crystalline phase of the LLZO thin films was investigated employing a grazing-incidence X-Ray diffractometer (GI-XRD) system (Bruker D8 Discover), using Cu Kα radiation at an incident angle ω = 2° and measuring the diffracted radiation in the range 2θ = 10 – 60°. Phase identification and Rietveld refinements of the lattice constants were performed using the open-source software Profex.[52]

The film morphology was studied from cross section and top view images acquired with a scanning electron microscope (SEM) (Hitachi FEG-SEM S-4800). The cross sections were prepared by cleaving the single-crystal substrate with cleaving pliers. The samples were coated with 3 nm of Pt to avoid charging during imaging.

Elemental characterization of the sample’s structure was performed using time-of-flight secondary ion mass spectrometry (TOF-SIMS). A high vacuum compatible compact TOF detector (CTOF[53,54] from TOFWERK) was integrated within a focused ion beam/scanning electron microscopy (FIB/SEM) multi-analytical tool Lyra (Tescan). Prior to the measurements, the samples were coated with a 5 nm thick Au layer.

### Table 4. Effective ionic conductivity at room temperature and activation energy for Ga-doped LLZO thin films annealed at different temperatures.

| Annealing temp. [°C] | σeff [S cm⁻¹] | Ea [eV] |
|----------------------|--------------|---------|
| 500                  | 10⁻⁹ (extrapolated) | 0.86 |
| 600                  | 3.54(18) × 10⁻⁵   | 0.38 |
| 700                  | 1.91(4) × 10⁻⁴    | 0.38 |
| 800                  | 3.13(38) × 10⁻⁷   | 0.54 |

microstructure, elemental structure, and ionic conductivity) and compared them to non-doped films. Besides the stabilization of the highly-conductive cubic phase, these dopants also assist in the densification of the films and improve the stability of the material in air.

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to counteract accumulation of charges. The sample surfaces were bombarded with a 30 keV mono-isotopic continuous $^{60}$Ga beam which was used for sputtering and imaging. Around 110–115 pA ion current, 100 μm aperture and 10 μs dwell time were used. The beam scanned over 10 $\times$ 10 μm$^2$ areas with 512×512 pixels and 2 $\times$ 2 binning. However, in order to prevent the edge induced artifacts (such as material re-deposition), only the central 5 $\times$ 5 μm$^2$ regions were considered for generating the elemental depth profiles. All data sets were mass-calibrated using the most prominent isotopes of the thin film ($^7$Li), substrate ($^{24}$Mg), and source ($^{60}$Ga).

Impedance spectroscopy (IS) and DC polarization curves were measured in an in-plane configuration. Au contacts with a thickness of 100 nm and a parallel spacing of 200 μm were thermally evaporated (Nexdep, Angstrom Engineering) on the annealed films. The complex impedance was measured from 10 Hz to 10 MHz with an amplitude of 50 mV using a Paios measurement system (Fluxim AG) and the data was fitted using Fluxim’s Characterization Suite software. DC polarization curves were measured by applying a constant potential of 0.5 V and the temperature was calibrated using the most prominent isotopes of the thin film ($^7$Li), substrate ($^{24}$Mg), and source ($^{60}$Ga).

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.

Keywords
ionic conductivity, lithium garnet, LLZO, solid electrolytes, solid-state batteries, thin films

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