# Densification and lithium ion conductivity of garnet-type $Li_{7-x}La_3Zr_{2-x}Ta_xO_{12}$ ($x = 0.25$) solid electrolytes*

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The garnet-type $Li_7La_3Zr_2O_{12}$ ceramic is a promising solid electrolyte for all-solid-state secondary lithium batteries. However, it faces the problem of lithium volatilization during sintering, which may cause low density and deterioration of ionic conductivity. In this work, the effects of sintering temperature and addition on the density as well as the lithium ion conductivity of $Li_{7-x}La_3Zr_{2-x}Ta_xO_{12}$ (LLZTO, $x = 0.25$) ceramics prepared by solid state reaction have been studied. It is found that optimization of the sintering temperature leads to a minor increase in the ceramic density, yielding an optimum ionic conductivity of $2.9\times10^{-4}$ S·cm$^{-1}$ at 25 °C. Introduction of $Li_3PO_4$ addition in an appropriate concentration can obviously increase the density, leading to an optimum ionic conductivity of $7.2\times10^{-4}$ S·cm$^{-1}$ at 25 °C. This value is superior to the conductivity data in most recent reports on the LLZTO ceramics.

**Keywords:** garnet electrolyte, sintering temperature, sintering addition, ionic conductivity

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## 1. Introduction

Recently, intensive research has been carried out on solid state lithium ion conductors because of their advantages over the presently used liquid organic electrolytes in terms of safety issues, such as dendrite formation, flammability, and leakage problem.[1–3] However, in real applications, especially the improvement of the lithium ion conductivity while maintaining the chemical and electrochemical stabilities,[2,4] many factors need to be considered.[5–10]

A new garnet-type electrolyte with a nominal chemical composition of $Li_7La_3Zr_2O_{12}$ (LLZO) has arisen as a new star recently because of its high ionic conductivity ($> 10^{-4}$ S·cm$^{-1}$), stability against lithium anodes, and large electrochemical window (about 9 V).[4,11–13] It may have a cubic or tetragonal phase dependent on the sintering temperature.[14–16] The former phase shows a conductivity two orders of magnitude greater than the latter, while the sintering temperature above 1200 °C is needed.[11,14,16–19] This may cause formation of pyrochlore $La_2Zr_2O_7$ and a decrease of the ceramic density, which have deterious effects on the lithium ion conductivity.[12] Thus, to solve these problems while maintaining the cubic phase, substitution of Zr by Al, Ta, Nb, Y, Si, In, or Ge has been studied.[3,11,12,18,20–25] It has been proved that the Ta substitution for Zr is preferred, owing to the following three reasons: (i) Ta is inert to lithium metal;[26] (ii) it can stabilize the cubic garnet structure at a relative lower sintering temperature;[21] (iii) it can lower the lithium content, thus increasing the lithium vacancy concentration, which is beneficial to the enhancement of lithium ion conductivity.[27] In $Li_{7-x}La_3Zr_{2-x}Ta_xO_{12}$, Wang and Lai[21] found that the maximum bulk or total conductivity appeared at $x$ in between 0.2 and 0.3. Therefore, we select the stoichiometry of $Li_{7-x}La_3Zr_{2-x}Ta_xO_{12}$ ($x = 0.25$) (LLZTO) for the investigated ceramics. Given that the optimum sintering condition has not yet been investigated, we systematically study the effects of sintering temperature on density and conductivity of the prepared samples. Moreover, it is known that $Li_3PO_4$ can be used as a sintering aid because of its low melting point of 837 °C as well as ionically conducting property. It may act as a binder between the grains to improve the ceramic density. Therefore, LLZTO with $Li_3PO_4$ in different addition concentrations are further studied. Effects of $Li_3PO_4$ additions on phase, sinterability, microstructure, and conduction behavior are analyzed. Enhancement of the lithium-ion conduction by the improved ceramic density is demonstrated.

## 2. Experimental details

$LiOH{\cdot}H_2O$ (Alfa Aesar, 98%), $La(OH)_3$ (Aladdin, 99.99%), $ZrO_2$ (Aladdin, 99.99%), and $Ta_2O_5$ (Aladdin, 99.99%) were used as starting materials to prepare LLZTO. The stoichiometric ratio of Li, La, Zr, and Ta was set as 7.76:3.00:1.75:0.25 with 15% excess of $LiOH{\cdot}H_2O$ added to compensate Li loss during sintering. These precursors were ball milled with agate balls for 24 h in isopropanol and presintered at 950 °C for 12 h. After this process, a small amount of residual tetragonal phase was left, which could be converted

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to the cubic phase by further ball milling for 24 h. $Li_3PO_4$ (Aladdin, 99.99%) in the concentration range of 1–6 wt% was added to the exclusive cubic LLZTO powders which were subsequently proceeded by repeated ball milling. The $Li_3PO_4$-added powders were pressed into pellets with diameters of 15 mm under a cold isotactic condition of 200 MPa. The LLZTO pellets without additives were sintered at 1150, 1175, 1200, and 1225 °C for 36 h. Those with 1–2 wt% $Li_3PO_4$ were sintered at 1175 °C for 6 h, and those with 4–6 wt% $Li_3PO_4$ at 1150 °C for 6 h. The sintering atmosphere is air. During sintering, the pellet was covered with the mother powder in order to compensate the loss of Li. The heating rate was 3 °C/min before 1000 °C and 2 °C/min after 1000 °C, while the cooling rate is 3 °C/min.

Powder X-ray diffraction (XRD, Bruker D8, Cu $K_\alpha$) was used to characterize the phase structure in the $2\theta$ range from 10° to 80°. The composition of the LLZTO samples was analyzed using inductively coupled plasma optical emission spectrometry (ICP-OES). Scanning electron microscopy (SEM, Hitachi S-3400N) was employed to observe the cross-sectional microstructure of the pellets. Archimedes' method was used to evaluate the relative density of the pellet. Electrical conductivity measurement was performed with a beta high-performance impedance analyzer (Novocontrol Technologies, Germany). For this measurement, the pellets were polished to as thin as 1 mm. Then, lithium foils were pressed on each side of the pellet in a glove box filled with Ar. The applied voltage was 10 mV, and the test frequency ranges from 30 M to 1 Hz. Direct current (DC) polarization measurement was conducted with Arbin instrument. Au pastes were painted on the pellet surfaces as electrodes, and heated at 800 °C for 10 min.

## 3. Results and discussion

As described in Section 2, the LLZTO ceramics without additions were prepared using the powder materials in cubic phase. After sintering at different temperatures, crystallography, density, and transport properties of these ceramics are investigated. Figure 1 shows the XRD patterns for the ceramics sintered at temperatures from 1150 to 1225 °C with the same sintering time of 36 h. The diffraction peaks fitting well to the structure of cubic $Li_5La_3Nb_2O_{12}$ (i.e., JCPDS: 80-0457) clearly indicate that the samples prepared in this temperature range are cubic. Similar to Ref. [3], a small amount of Al-containing impure phase from the $Al_2O_3$ crucibles is detected. The ICP-OES chemical analysis reveals that the atomic percentage of Li/La/Zr/Ta is approximately 0.70/3.35/2.0/0.28 (instead of 0.75/3.0/1.75/0.25), indicating a slight Li deficiency and La and Zr excess with respect to the nominal composition. It can be concluded that the temperature from 1150 to 1225 °C is good for preparing the cubic LLZTO. As the sintering temperature further increases to 1250 °C, the pyrochlore phase appears, which should be avoided owing to its detrimental effect on ion conduction.

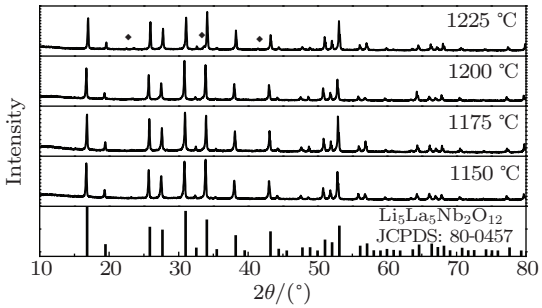



**Fig. 1.** XRD patterns for LLZTO ceramics sintered at different temperatures. The symbol ♦ denotes a small amount of $LaAlO_3$ impure phase coming from the crucible used.

Measurement of the relative density reveals that these samples have densities from 88.9% to 89.8%, as given in Table 1. The one sintered at 1175 °C shows a relatively larger density (i.e., 89.8%). Cross-sectional SEM images provide consistent results, as shown in Fig. 2. Many pores can be observed in between as well as inside the grains. The grain size is as large as 60–70 μm. These features are related to Li volatilization in combination with the long sintering time at these temperatures, which may cause the formation of pores and anomalous growth of grains.[25]

**Table 1.** Sintering condition, optimum relative density, overall conductivity at room temperature, activation energy and electronic conductivity at room temperature of all the samples.

| $Li_3PO_4$ amount/wt% | Sintering condition | Optimum relative density/% | Overall conductivity/$10^{-4}$ S·cm$^{-1}$ | Activation energy/eV | Electronic conductivity/$10^{-7}$ S·cm$^{-1}$ |
|---|---|---|---|---|---|
| 0 | 1150 °C, 36 h | 88.9 | 1.6 | 0.45 | – |
| | 1175 °C, 36 h | 89.8 | 2.9 | 0.42 | 24.2 |
| | 1200 °C, 36 h | 89.2 | 2.4 | 0.43 | – |
| | 1225 °C, 36 h | 89.6 | 2.0 | 0.42 | – |
| 1 | 1175 °C, 6 h | 92.7 | 7.2 | 0.42 | 19.4 |
| 2 | 1175 °C, 6 h | 92.1 | 4.7 | 0.48 | 7.11 |
| 4 | 1150 °C, 6 h | 90.1 | 3.1 | 0.46 | 6.95 |
| 6 | 1150 °C, 6 h | 89.3 | 1.6 | 0.46 | 6.76 |

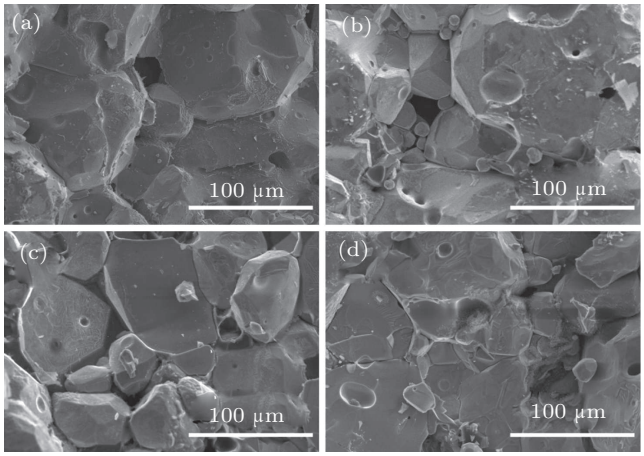



**Fig. 2.** Cross-sectional SEM images for LLZTO pellet sintered at (a) 1150 °C, (b) 1175 °C, (c) 1200 °C, and (d) 1225 °C for 36 h.

Impedance spectroscopy (IS) measurement was carried out on the above samples. The lithium foils pressed on the surfaces of pellets were used as the electrodes. The obtained data are given by Cole–Cole plots, as shown in Fig. 3. A partial semicircle in the relatively high frequency range (27 M to 1 MHz) can be clearly seen for each sample, which can be attributed to the overall resistivity of the sample. The large tail in the low-frequency range ($\leq$ 1 MHz) is attributed to the impedance resulting from the interface between the electrode and the sample. It can be found that the one sintered at 1175 °C exhibits a smaller overall resistivity (as listed in Table 1), correlating well with its larger relative density.

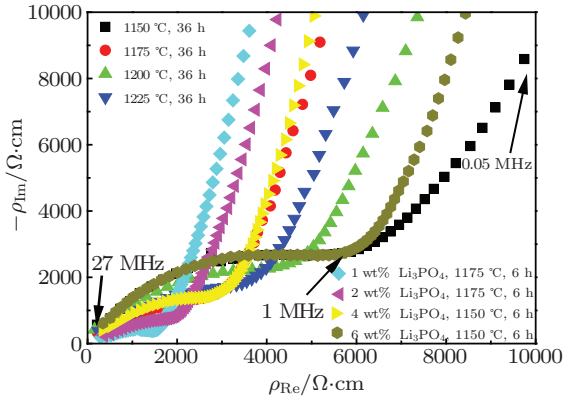



**Fig. 3.** Nyquist plots of all the LLZTO pellets sintered at different temperatures and incorporated with various amount of $Li_3PO_4$ addition. Measurement was performed at room temperature. Resistivity $\rho$ was calculated by the expression $\rho = Rs/L$, where $R$ is the measured resistance, $L$ is the thickness of the ceramic pellet, and $s$ is the electrode area.

Based on the above impedance data, conductivity as a function of temperature was investigated. According to the Arrhenius law, $\sigma T = A\exp(-E_a/kT)$, where $\sigma$ is the electrical conductivity, $T$ is the absolute temperature, $A$ is the pre-exponential factor, $E_a$ is the activation energy, and $k$ is the Boltzmann constant. The values of $E_a$ are calculated and listed in Table 1. It can be seen that these values are comparable to that of the previously reported Ta-doped garnet $Li_6La_3ZrTaO_{12}$ (0.42 eV).[22]

The above results indicate that the conductivity can be increased by optimizing the sintering temperature, even if the improvement effect is minor. In order to further improve the conductivity of LLZTO, we used $Li_3PO_4$ as sintering additions, and studied their effects on the densification and lithium ion conductivity.

Figure 4 shows the XRD patterns of the LLZTO added with different amounts of $Li_3PO_4$. It can be found that all the patterns match well with the standard pattern of the cubic $Li_5La_3Nb_2O_{12}$. A small amount of Al-containing impure phase is also observed. Figure 5 displays the SEM images for the cross sections of the ceramics with added $Li_3PO_4$. First of all, it can be clearly observed that the average size of grains (i.e., 6–7 μm) is ten times smaller than that (i.e., 60–70 $\mu$m) of the LLZTO without $Li_3PO_4$ (Fig. 2). This means that the $Li_3PO_4$ addition suppresses the anomalous growth of the LLZTO grains related to the Li volatilization.[25] Second, no pores can be observed in between as well as inside the grains. Analysis of chemical composition through energy dispersive X-ray spectroscopy (EDS) reveals that the phosphorus phase only distributes at the grain boundaries. The measured concentration of $Li_3PO_4$ is approximately 5 wt% for the sample added with 6 wt% nominal $Li_3PO_4$. More detailed data corresponding to the regions marked by the white points in Fig. 5(d) are listed in Table 2. These results clearly indicate that the $Li_3PO_4$ behaves as the binder to reduce the residual pores therein. The relative density listed in Table 1 indicates that the relative densities of the LLZTO with $Li_3PO_4$ increase remarkably when the $Li_3PO_4$ concentration is 1 wt%, while decrease as the concentration increases further. Based on these results, it can be concluded that the introduction of appropriate amount of $Li_3PO_4$ can improve the ceramic density through the reduction of pores and suppression of anomalous grain growth. Note that the LLZTO pellets with different concentrated $Li_3PO_4$ show different optimum sintering temperature in terms of maximum relative density. The sintering temperature

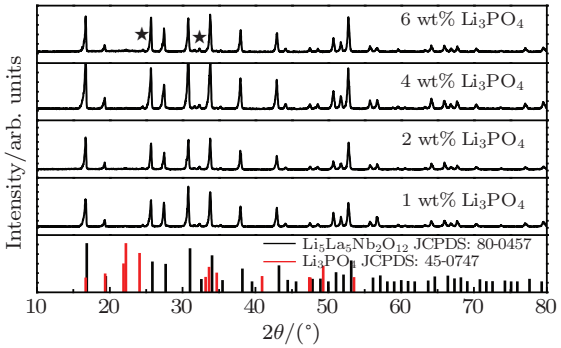



**Fig. 4.** XRD patterns for LLZTO incorporated with varying amount of $Li_3PO_4$ addition. The symbol ★ denotes a small amount of $La_2Li_{0.5}Al_{0.5}O_4$ impure phase coming from the used crucible.

of 1175 °C is found to be the optimum sintering temperature for the pellets with 1 wt% and 2 wt% $Li_3PO_4$, while that of 1150 °C for the pellets with 4 wt% and 6 wt% $Li_3PO_4$. Moreover, it can be found that $Li_3PO_4$ addition leads to an obvious decrease of the sintering time. Just after sintering for 6 h, the ceramics exhibit higher densities than those without additions which would need much longer sintering time to achieve the same densities. These results imply that $Li_3PO_4$ may form a liquid phase during sintering concerning its low melting point.

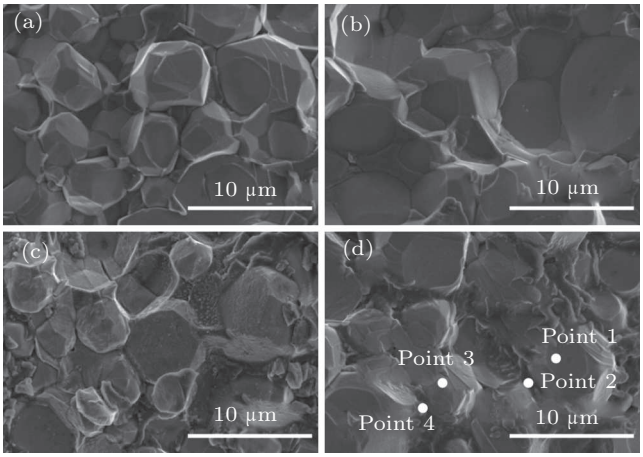



**Fig. 5.** Cross-sectional SEM images of LLZTO ceramics with (a) 1 wt%, (b) 2 wt%, (c) 4 wt%, and (d) 6 wt% $Li_3PO_4$ addition.

**Table 2.** EDS results of the points marked by the white points in the SEM (at%).

| | La | Zr | Ta | O | P | $Li_3PO_4$/wt% |
|---|---|---|---|---|---|---|
| Point 1 | 22.00 | 13.08 | 1.64 | 63.27 | 0.00 | – |
| Point 2 | 23.35 | 9.52 | 1.11 | 63.40 | 2.62 | 5.05 |
| Point 3 | 22.50 | 12.42 | 1.85 | 63.23 | 0.00 | – |
| Point 4 | 28.50 | 5.44 | 0.98 | 62.51 | 2.57 | 4.96 |

The conduction properties for all the $Li_3PO_4$-added samples in the Cole–Cole plot are shown in Fig. 3. The Arrhenius relations for all the samples are shown in Fig. 6. The values of the optimum relative density, conductivity, and activation energy are summarized in Table 1. In comparison to those for the LLZTO samples without the additions, the total conductivity of the sample with 1 wt% $Li_3PO_4$ addition obviously increases. As the amount of $Li_3PO_4$ increases, the conductivity decreases gradually. Overall, all the $Li_3PO_4$-added pellets, except the 6 wt% one, show higher total lithium ion conductivities. The maximum value of $7.2\times10^{-4}$ S·cm$^{-1}$ is shown by the ceramic incorporated with 1 wt% $Li_3PO_4$. This result is consistent with the density and microstructural results. Through an appropriate addition, a considerable improvement of densification can be achieved, leading to grains fused together and an easy migration of lithium ions between the grains. However, the total conductivity decreases as the amount of $Li_3PO_4$ increases to 6 wt%. $Li_3PO_4$ itself has a very low ionic conductivity of about $10^{-7}$–$10^{-8}$ S·cm$^{-1}$ even at a high temperature of 300 °C,[28] which is much lower than that of LLZTO. Too much $Li_3PO_4$ addition may form nets at the grain boundaries, which blocks the lithium ion migration. Consequently, 1 wt% $Li_3PO_4$ addition improves the transport properties of the ceramics. The above assumptions are supported by the calculated activation energies. As listed in Table 1, with 1 wt% $Li_3PO_4$ addition, the $E_a$ values do not change remarkably. This indicates the increased conductivity is attributed to the improved connection between the LLZTO grains instead of the second phase at the grain boundaries. The $E_a$ increases with increasing $Li_3PO_4$ addition amount, indicating that the additions are involved as the pathway of the ion transport.

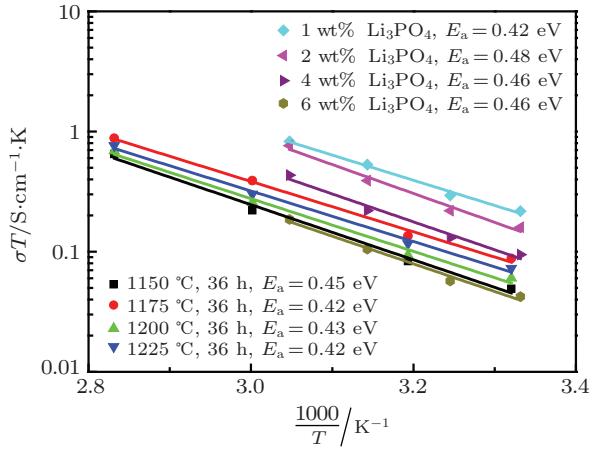



**Fig. 6.** Arrhenius plots of the total conductivity for the LLZTO ceramics sintered at different temperatures and those incorporated with various amount of $Li_3PO_4$ addition.

In order to check the electronic conductivities of the above samples, galvanostatic polarization measurement was carried out with Au electrodes. Every measured curve shows an exponential relation between voltage and time, indicating a typical ionically conducting behavior. The obtained electronic conductivities according to the equilibrium potential are given in Table 1. It can be seen that for all the samples, the ionic conductivity is at least two orders of magnitude larger than the electronic counterpart, clearly indicating that the investigated ceramics are ionically conducting materials.

## 4. Conclusion

The efects of sintering temperature and $Li_3PO_4$ addition on density and conduction properties of LLZTO electrolytes synthesized by solid state reaction have been studied. The optimized sintering temperature leads to a minor increase of ceramic density as well as ionic conductivity. Through $Li_3PO_4$ addition, the sintering time is greatly reduced from 36 h to 6 h. Meanwhile, the grains become much smaller and better connected. These features lead to the total lithium ion conductivity reaching $7.2\times10^{-4}$ S·cm$^{-1}$ in the sample incorporated

with 1 wt% $Li_3PO_4$. This value is superior to the conductivity data in most recent reports.[21–23] The results demonstrate that $Li_3PO_4$ of an appropriate amount acts as a sintering binder and is beneficial to ion conduction of the LLZTO electrolytes.

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