Spark plasma sintering plus heat-treatment of Ta-doped Li$_7$La$_3$Zr$_2$O$_{12}$ solid electrolyte and its ionic conductivity

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Abstract
Ta-doped Li$_7$La$_3$Zr$_2$O$_{12}$ (Ta-LLZO) solid electrolyte ceramics were synthesized by solid-state sintering, spark plasma sintering (SPS) and SPS plus heat-treatment (two-step method) using LiOH-H$_2$O, La$_2$O$_3$, ZrO$_2$ and Ta$_2$O$_5$ as the raw materials. The Ta-LLZO samples prepared from these three routes are all in cubic phase structure. However, the solid-state method results in Ta-LLZO samples with different particle sizes and porous morphology, while the samples prepared by SPS route contain fewer internal voids and smaller particle size. The two-step method not only retains the high compactness of SPS samples, but also the increment of grain size. The SEM results demonstrate that Ta-LLZO sintered by the two-step method shows optimal electrical properties. And the total ionic conductivity is 4.6 × 10$^{-3}$ S cm$^{-1}$ at 150 °C and the activation energy is calculated to be 0.38 eV.

1. Introduction
Lithium-ion battery has drawn great attention due to its high voltage, small volume, low weight, high energy density, non-memory effect, low self-discharge and long cycle life [1–3]. However, the safety issues remain a major challenge for lithium-ion batteries using traditional liquid electrolytes. Based on the advantages in safety and energy density, all solid-state batteries (ASSBs) have become the only way to develop lithium batteries in the future [4–6]. Compared with conventional lithium ion batteries, the potential advantages of ASSBs include their high energy density, simple structure, high safety and reliability [7, 8]. However, there are still some limitations in the application of solid electrolytes, such as the solid-solid interface between electrodes and electrolytes, as well as the relatively low ionic conductivity.

Solid electrolytes can be divided into inorganic solid electrolytes and polymer electrolytes according to their composition. Garnet-type solid electrolyte has attracted extensive attention because of its promising electrochemical performance. Li$_7$La$_3$Zr$_2$O$_{12}$ with a cubic crystal structure generally exhibits relatively high ionic conductivity. However, this material easily decomposes into tetragonal phase or La$_2$Zr$_2$O$_7$ during high temperature heat treatment [9–11]. The ionic conductivity of tetragonal phase is two orders of magnitude lower than that of cubic phase. However, the cubic phase can be effectively stabilized under elevated sintering temperature in the synthesis process. To obtain stabilized cubic phase Li$_7$La$_3$Zr$_2$O$_{12}$, the sintering temperature is generally higher than 1000 °C, which also evokes serious lithium volatilization problems [12].

At present, the synthesis of solid electrolyte Li$_7$La$_3$Zr$_2$O$_{12}$ is mainly conducted using solid-state and sol-gel routes [13–15]. Solid-state method is widely used because of its low cost and simple operation. Its disadvantages are the low reactivity of powder and high energy consumption. Due to the high temperature sintering in solid-state synthesis, the lithium volatilization will lead to the instability of crystal structure and poor sintering performance [9]. At the same time, the non-conductive La$_2$Zr$_2$O$_7$ will be produced, which will dramatically reduce the ionic conductivity [16]. On the other hand, to ensure the formation of cubic structure and...
densification of Li$_7$La$_3$Zr$_2$O$_{12}$ electrolyte samples, high temperature sintering under long time is needed and lithium volatilization can hardly be eliminated. On the contrary, the sol-gel method requires lower sintering temperature and uniform doping at the molecular level. Kotobuki et al. have prepared Li$_7$La$_3$Zr$_2$O$_{12}$ precursor powders by sol-gel method and garnet electrolyte after sintering at 1100 °C for 6 h, which exhibits cubic structure and high ionic conductivity of 1.5 × 10$^{-4}$ S cm$^{-1}$ [17]. However, the sol-gel method results in much higher cost of the raw reactants and much longer time of the synthesis process. Therefore, other innovative sintering techniques have been proposed to overcome these drawbacks, such as spark plasma sintering (SPS) [18–20], hot-press sintering [21] and chemical precipitation method [22, 23]. Compared with conventional sintering route, SPS can be performed at a lower temperature and shorter time duration (within 1–10 min), which can successfully prepare garnet electrolyte without any sintering additives [24, 25]. SPS has been widely used to prepare a variety of conducting and non-conducting materials including lithium ion conductors, such as NASICON-type LiTi$_2$(PO$_4$)$_3$ and LiHf$_2$(PO$_4$)$_3$ [19, 20], as well as perovskite-type Li$_{1−x}$La$_2$/3−xTiO$_4$ [26].

In this study, we have explored the synthesis of garnet electrolyte Ta-doped Li$_7$La$_3$Zr$_2$O$_{12}$ (Ta-LLZO) using solid-state sintering, SPS and SPS plus heat-treatment routes. The heat-treatment process was introduced on the basis of SPS densification, which is beneficial to further promote the bulk density and grain size. It’s known that voids and grain boundaries are very harmful for ion conductivity. Thus, the elevated grain size is expected to reduce the grain boundary surface and improve the ion conductivity. The effect of grain size on the ion conductivity was explored. The phase composition, microstructure and ionic conductivity analysis using different synthesis routes were investigated as well.

2. Experimental details

2.1. Preparation of Ta-LLZO pellets

Raw powders of LiOH, La$_2$O$_3$, Ta$_2$O$_5$ and ZrO$_2$ were purchased from Aladdin Biochemical Technology Co. Ltd as the raw materials, which were mixed with the corresponding molar ratio to produce the target product (Li$_7$La$_3$Zr$_2$O$_{12}$). In order to compensate for the loss of lithium under high temperature sintering, 10 wt% excess of lithium hydroxide was added. The weighed samples were ball-milled for 12 h with isopropanol as the dispersing reagent. The mixture was dried in oven and then pressed into cylinder pellets at 20 MPa, which were calcined at 900 °C for 6 h to form the initially tetragonal LLZO phase. The calcined pellets were ground again and re-pressed into pellets for next calcination at different temperatures (1150 °C–1200 °C) and dwelling times (6–24 h). The whole calcination process was conducted with the pellets be imbedded in mother powder.

The two-step process includes spark plasma sintering (SPS) and heat-treatment in air. The preparation of pre-sintered powder is the same as that of the previous solid phase method. The different sintering schedule is shown in table 1. SPS sintering was carried out on the pre-sintered powder, in which the heating rate was 50 °C/min with 40 MPa pressure and 5 min holding time. The sintering temperature was fixed to be 800 °C. The graphite on the sample surface was treated and then subjected to high temperature heat treatment, which was imbedded in mother powder under sintering in air. Compared with the two-step method, the solid phase method was conducted at 1175 °C with 12 h for the preparation of LLZO pellets.

2.2. Characterizations

The structure and composition of calcined powders and pellets were analyzed using x-ray diffractometer (XRD, X’ Pert PRO, PANalytical B V, Netherlands) with a copper anode (Cu Kα radiation, λ = 1.54187 Å). The morphology of sintered pellets were observed by scanning electron microscope (SEM, Ultra55, Carl zeiss, Germany). AC impedance spectroscopy measurement was conducted on an Agilent 4294 A electrochemical workstation to determine the ionic conductivity of the pellets. The polished pellets were pasted by Ag electrode on both surfaces and loaded into a Swagelok cell in Ar-glovebox to exclude the adverse influence of air/moisture on conductivity measurement. The measurements were performed by applying 10 mV in the frequency range of 1 MHz-100 Hz in the temperature range from 30 °C to 150 °C. The ionic conductivity of solid electrolytes is calculated using equation (1):

Table 1. Different sintering schedule.

|                  | Solid-state sintering | SPS       | Two-step process |
|------------------|------------------------|-----------|------------------|
| Temperature (°C) | 1150–1200              | 800       | 1175             |
| Holding time     | 6–24 h                 | 5 min     | 12 h             |
| Cooling mode     | With furnace cooling   | With furnace cooling | With furnace cooling |
where $\sigma$, l and D represent the ionic conductivity, thickness and diameter of solid electrolytes and $R$ refers to the impedance value obtained from the impedance spectra, respectively. The activation energy of solid electrolytes is calculated by the following equation (2):

$$\sigma = \sigma_0 \exp \left( -\frac{E_a}{kT} \right)$$

where $\sigma_0$, $E_a$ and $K$ are pre-exponential ionic conductivity, activation energy and Boltzmann’s constant, respectively.

### 3. Results and discussion

The sintering temperature exhibits an important influence on the densification of solid electrolytes. For garnet $Li_7La_3Zr_2O_{12}$ solid electrolyte, the suitable sintering temperature also means the phase transformation from tetragonal phase to cubic phase. Figure 1 shows the XRD results of LLZO pellet after solid-state sintering at 1150 °C, 1175 °C and 1200 °C for 6 h. It can be clearly seen from the diagram that the LLZO phase gradually transforms from tetragonal phase to cubic phase with the increase of sintering temperature. In order to compensate for lithium volatilization at high temperature, 10 wt% excessive lithium and burial sintering in mother powder were utilized in this experiment, resulting in the emergence of impurity $Li_2ZrO_3$ phase. According to this result, 1175 °C was selected as the optimal sintering temperature of LLZO.

Figure 2 shows the AC impedance plots of LLZO at 30–150 °C and its Arrhenius curve. The corresponding ionic conductivities were calculated as shown in table 2. The total impedance of electrolyte sheet decreases with the increase of testing temperature, which indicates that the increase of temperature makes the conductible lithium ion with higher energy and can break through the barrier needed for migration. However, when the temperature exceeds 120 °C, the total impedance decreases slightly, which indicates that the lithium ion at this temperature has enough energy to migrate, and the temperature shows little effect on the ionic conductivity of the sample. The activation energy of 1175 °C sintered LLZO pellet was calculated to be 0.41 eV.

Ta-doped $Li_7La_3Zr_2O_{12}$ (Ta-LLZO) is deemed as a promising inorganic solid electrolytes. Figure 3 presents the XRD patterns of Ta-LLZO samples obtained by the three synthesis methods. It can be concluded that all the three samples maintain the cubic phase structure. However, the impurity $La_2Zr_2O_7$ phase was formed in SPS method due to the volatilization of lithium. On the other hand, the impurity $Li_2ZrO_3$ phase was produced in the two-step route, which may be related with the excessive Li content in the sintering process and burial sintering in mother powder. $Li_2ZrO_3$ phase is also a conductive phase of lithium, which is not very harmful for the ion conductivity. This result shows that the formation of non-conductive phase $La_2Zr_2O_7$ can be inhibited by the burial sintering in mother powder and the existence of excessive lithium dopant.

The total impedance of SPS sintered LLZO samples is obviously divided into grain impedance and grain boundary impedance as shown in figure 4. The grain conductivity and total conductivity of Ta-LLZO samples sintered by SPS are measured to be $1.2 \times 10^{-5}$ S cm$^{-1}$ and $7.6 \times 10^{-6}$ S cm$^{-1}$, respectively. The total
Figure 2. (a) AC impedance plots of LLZO at 30°C–150°C; (b) Arrhenius curve of LLZO sample.

Table 2. Ion conductivity of undoped LLZO at different temperatures.

| Temperature (°C) | 30     | 60     | 90     | 120    | 150    |
|------------------|--------|--------|--------|--------|--------|
| Ion conductivity (S cm⁻¹) | 4.12 × 10⁻⁵ | 1.13 × 10⁻⁴ | 8.27 × 10⁻⁴ | 1.65 × 10⁻³ | 3.25 × 10⁻³ |

Figure 3. XRD pattern of Li₆.5La₃Zr₁.5Ta₀.5O₁₂ under different synthesis methods.

Figure 4. AC impedance plots of Ta-LLZO: (a) SPS, (b) two-step method.
The conductivity of the sample obtained by two-step method is $2.9 \times 10^{-4}$ S cm$^{-1}$. Compared with the Li$_6.5$La$_3$Zr$_1.5$Ta$_0.5$O$_{12}$ electrolyte sheet ($6.9 \times 10^{-4}$ S cm$^{-1}$, $25^\circ$C) synthesized by SPS sintering [27], the ionic conductivity of Ta-LLZO electrolyte sheet obtained in this experiment is much lower. The decrement of ionic conductivity is mainly attributed to the formation of more non-conductive phase La$_2$Zr$_2$O$_7$, which reduces the whole ionic conductivity dramatically. It is obvious that the ionic conductivity of SPS samples has been greatly improved after subsequent heat-treatment.

As can be seen from figure 5 and table 3, the ionic conductivity of the two-step synthesized Ta-LLZO sample exhibits a similar trend as that of the undoped LLZO sample mentioned above. The total ionic conductivity is significantly promoted as the $30^\circ$C value is $9.58 \times 10^{-5}$ S cm$^{-1}$. With the increase of testing temperature, the total resistance decreases and the ionic conductivity of the sample increases accordingly. The activation energy of Ta-doped LLZO was calculated to be 0.38 eV, which is lower than that of the undoped LLZO sample. The decrease of activation energy means that the energy required for lithium ion migration decreases and the ionic conductivity increases.

Figure 6 shows the SEM images of Ta-LLZO under different sintering methods. The size of the samples sintered by solid-state method is uneven and the voids between the particles are large, which means the relative density is low. However, the sample sintered by SPS exhibits small and uniform grains with grain size of 3–6 $\mu$m and compact distribution among the particles. Obviously, the density of the samples sintered by two-step method is much higher than that of the samples sintered without pressure. The grain size of the samples sintered by two-step method is much larger than that of the samples sintered by single SPS method. The grain size is about 10–15 $\mu$m and arranged compactly with almost no pore between the particles. It can be concluded that the Ta-LLZO samples obtained by SPS sintering at 1175 $^\circ$C for 12 h have the advantages of large grain size, less porosity and high compactness in microstructure. This phenomenon indicates that the density does not always decrease with the increase of grain size, which has also been testified in the previous reports [28, 29]. It can be concluded that the Ta-LLZO sample obtained by two-step method have the advantages of large grain size, less porosity and high compactness in microstructure.

### 4. Conclusions

Ta-LLZO ceramics were synthesized by three routes of high temperature solid-state method, SPS and SPS plus heat-treatment. From the XRD results, phase compositions of the three samples obtained from these routes are very similar. But the microstructure of solid-state sintered Ta-LLZO samples shows different particle size and more voids. The inner voids of the SPS sintered Ta-LLZO samples are much fewer, and the particle size is uniform and smaller. The two-step method not only retain the high compactness of SPS sample, but also promotes the grain size. These microscopic characteristics are also reflected by their ionic conductivity.

![Figure 5](image.png)

**Figure 5.** (a) AC impedance plots of two-step synthesized Ta-LLZO at 30 $^\circ$C–150 $^\circ$C, (b) Arrhenius curve of Ta-LLZO.

| Temperature ($^\circ$C) | 30 | 60 | 90 | 120 | 150 |
|------------------------|----|----|----|-----|-----|
| Ion conductivity (S cm$^{-1}$) | $9.58 \times 10^{-5}$ | $3.54 \times 10^{-4}$ | $1.15 \times 10^{-3}$ | $2.30 \times 10^{-3}$ | $4.60 \times 10^{-3}$ |

Table 3. Ion conductivity of two-step synthesized Ta-LLZO at different temperatures.
increase of density and grain size in the two-step method, the total ionic conductivity of Ta-LLZO samples is also elevated.

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References

[1] Armand M and Tarascon J M 2008 Building better batteries Nature 451 652–7
[2] Goodenough J B and Kim Y 2010 Challenges for rechargeable Li batteries Chem. Mater. 22 587–603
[3] Berecibar M et al 2015 Critical review of state of health estimation methods of Li-ion batteries for real applications Renew. Sust. Energ. Rev. 56 972–87
[4] Ohta N et al 2006 Enhancement of the high-rate capability of solid-state lithium batteries by nanoscale interfacial modification Adv. Mater. 18 2226–9
[5] Kobayashi T et al 2008 All-solid-state battery with sulfur electrode and thio–LISICON electrolyte J. Power Sources 182 621–5
[6] Kotobuki M et al 2010 Compatibility of Li2La2Zr2O12 Solid Electrolyte to All-Solid-State Battery Using Li Metal Anode J. Electrochem. Soc. 157 A1076–9
[7] Knauth P 2009 Inorganic solid Li ion conductors: An overview Renew. Sust. Energ. Rev. 180 911–6
[8] Fergus J W 2010 Ceramic and polymeric solid electrolytes for lithium-ion batteries J. Power Sources 195 4554–69

Figure 6. The SEM patterns of Ta-LLZO: (a) Solid-state sintering, (b) SPS, (c) Two-step method.
[9] Back S W et al 2014 Garnet related lithium ion conductor processed by spark plasma sintering for all solid state batteries J. Power Sources 249 197–206
[10] Wolfenstine J et al 2012 Synthesis and high Li-ion conductivity of Ga-stabilized cubic Li7La3Zr2O12 Mater. Chem. Phys. 134 571–5
[11] Deviannapoorani C et al 2013 Lithium ion transport properties of high conductive tellurium substituted Li7La3Zr2O12 cubic lithium garnets RSC Adv. 240 18–25
[12] Huang M, Liu T and Deng Y 2011 Effect of sintering temperature on structure and ionic conductivity of Li7-xLa3Zr2O12-0.5x (x=0.3–0.7) ceramics Solid State Ion. 204–205 11–5
[13] Li Y et al 2014 Densification and ionic-conduction improvement of lithium garnet solid electrolytes by flowing oxygen sintering J. Power Sources 248 642–6
[14] Kokal I I et al 2011 Sol-gel synthesis and lithium ion conductivity of Li7La3Zr2O12 with garnet-related type structure Solid State Ion. 185 42–6
[15] Toda S et al 2013 Low temperature cubic garnet-type CO2-doped Li7La3Zr2O12 Solid State Ion. 233 102–6
[16] Kali R and Mukhopadhyay A 2014 Spark plasma sintered/synthesized dense and nanostructured materials for solid-state Li-ion batteries: overview and perspective J. Power Sources 247 920–31
[17] Kobayashi Y et al 1999 Densification of LiTi2(PO4)3-based solid electrolytes by spark-plasma-sintering J. Power Sources 81-82 833–8
[18] David I N et al 2015 Microstructure and Li-ion conductivity of hot-pressed cubic Li7La3Zr2O12 J. Am. Ceram. Soc. 98 1209–14
[19] Chen F et al 2017 Effect of Mo6+ substitution on microstructure and lithium ionic conductivity of garnet-Type Li7La3Zr2O12 solid electrolytes by field assisted sintering technology Springer, Cham 115–23
[20] Mei A et al 2009 Lithium lanthanum titanium oxide solid-state electrolyte by spark plasma sintering J. Alloy. Compd. 486 871–5
[21] Yamada H, Ito T and Honghally B R 2016 Sintering mechanisms of high-performance garnet-type solid electrolyte densified by spark plasma sintering Electrochim. Acta 222 648–56
[22] Shao C Y et al 2016 Structure and ionic conductivity of cubic Li7La3Zr2O12 solid electrolyte prepared by chemical co-precipitation method Solid State Ion. 287 13–6
[23] Kim K W et al 2016 Cubic phase behavior and lithium ion conductivity of Li7La3Zr2O12 prepared by co-precipitation synthesis for all-solid batteries J. Ind. Eng. Chem. 36 279–83