Synthesis of Li$_7$La$_3$Zr$_2$O$_{12}$ Solid Electrolyte by Solid Phase Sintering Method

Guanghua Liu$^1$, Tianjun Li$^2$, Yan Xing$^3$ and Wei Pan$^1$*

State Key Laboratory of New Ceramics and Fine Processing, School of Materials Science and Engineering, Tsinghua University, Beijing, 100084, PR China.

1 liugh17@mails.tsinghua.edu.cn; 2 li-tj13@mails.tsinghua.edu.cn; 3 xingy14@mails.tsinghua.edu.cn; 5 panw@mail.tsinghua.edu.cn

Abstract. Li$_7$La$_3$Zr$_2$O$_{12}$ (LLZO) is a promising electrolyte material for all-solid-state battery due to its high ionic conductivity and good air stability with metallic lithium. In this article, Li$_7$La$_3$Zr$_2$O$_{12}$ electrolytes with excess lithium 4wt%, 6wt%, 8wt%, 10wt% were prepared by traditional two steps solid-phase sintering method. The influence of concentration of lithium and calcination temperature on the structure of Li$_7$La$_3$Zr$_2$O$_{12}$ were investigated by X-ray diffraction (XRD) and scanning electron microscopy (SEM) in detail. To improve the density of the sample, the granulation was applied. Scanning electron microscopy (SEM) results showed the granulation of Li$_7$La$_3$Zr$_2$O$_{12}$ powder before pressing can significantly accelerate densification during the final high temperature, long duration sintering process.

1. Introduction

Solid lithium fuel cell, due to its high ionic conductivity and safety characteristics, has been widely considered as next generation energy storage devices. LISICON, perovskite and garnet types are traditional electrolyte materials. Among them, garnet crystalline solid electrolyte is widely researched due to its stable to lithium metal, low raw material cost and high mechanical strength. Many advanced materials with garnet type have been investigated for the electrolytes, but the garnet type structure of LLZO exists in three phases: a high temperature (HT) cubic phase whose lattice parameter is approx. 12.98 Å with disordered lithium sites, a low temperature (LT) cubic phase whose lattice parameter is approx. 13.00 Å and a moderate temperature tetragonal phase whose Li sites are completely ordered with 100% occupancy, the conductivity of the cubic phase is two order of magnitude higher than that of the tetragonal [1]. Structural characterization and Li-conductivity studies have shown that there are two populations of lithium cations, nominally called octahedral (less tightly bound) and tetrahedral sites (tightly bound), cubic phase LLZO have a larger portion of Li octahedral site than tetragonal phase and the octahedrally coordinated lithium are considerably more mobile than the tetrahedrally coordinated lithium. Li contents and sintering temperature are vital for obtaining cubic LLZO phase, however, it is difficult to obtain pure cubic phase LLZO because cubic phase is restricted to the sintering temperature and it is troublesome to control the Li contents due to the loss of Li in the high temperature and long duration time. Up to now, numerous of approach has been used to enhance its conductivity [2-4].

In the recent years, remarkable technological progresses have been made in lithium solid state electrolytes by doping different cations, improving manufacturing process and developing new synthesis methods [5-10]. It is reported sintering temperature excess to 1180 °C and Li concentration of approximately 6.0 moles Li was required for cubic LLZO. Moreover, stabilization of cubic LLZO
through unintentionally incorporating Al by a reaction between the molten precursors and the alumina crucible wall during the heat treatment was first reported [11]. It has been suggested that substitution of small amounts of an atom in a substitutional solid solution can stabilize a given structure in pressure-temperature-compositional space and increase its conductivity at room temperature by decrease the Li site occupancies and permit increased Li ion mobility [12]. Since then, a series of cations (Fe$^{3+}$, Ga$^{3+}$, Nb$^{4+}$, Ta$^{5+}$, Te$^{6+}$, etc.) doped method was applied to stabilize cubic LLZO and obtained high ionic conductivities [13-17].

Microstructure and high relative density are another crucial factor for LLZO to improve the ionic conductivity. For example, pellets sintered in Pt crucibles were compact with high relative density (~96%); little grain boundary and porosity were observed and ionic conductivity can be reached to 4.48 $\times$ 10$^{-4}$ S cm$^{-1}$) [18]. Hot pressing has been used to minimize grain-boundary resistance. Hot-pressing, field-assisted sintering and other technologies have been studied to increase the density of LLZO bulk, like hot-pressing at 1100°C and fixed pressure (62 MPa), the cubic LLZO relative density was ~99% [19-20]. However, all of these efforts improve the density of LLZO at the expense of high production cost, which is large energy consuming and unsuitable for mass production[21]. However, all of these efforts improve the density of LLZO at the expense of high production cost, which is large energy consuming and unsuitable for mass production[20].

In our work, a traditional solid phase sintering method was used to prepare cubic LLZO pellet. Their structure and morphology were characterized by X-ray diffraction (XRD) and scanning electron microscopy (SEM). The LLZO powder was first prepared by adjusting different lithium concentration and calcination temperature, and the optimal conditions was discussed in detail. The pure cubic phase LLZO pellets were then obtained from granulation process under the guarantee of powdery purity at 1200 °C for 24 h with the mother powder buried it. The relative density was investigated by the electronic densimeter. By making the devices, we also measured the conductivity of the LLZO samples. We expect such an LLZO materials with ideal phase structure fabricated by relatively low energy-consuming fabrication procedure may find some application in energy storage devices.

2. Experimental procedure

2.1. The fabrication of LLZO
The cubic LLZO was synthesized by solid state sintering method, as shown in Fig.1a.In the typical experiment, ZrO$_2$ (99%, Shanghai McLean biochemical technology co., LTD), La$_2$O$_3$ (99.99% Shanghai McLean biochemical technology co., LTD), Li$_2$CO$_3$ (99%, Shanghai Aladdin biochemical technology co., LTD) and Al$_2$O$_3$(99%, Shanghai Aladdin biochemical technology co., LTD) were used as the starting materials. La$_2$O$_3$ was first heated at about 1273 K for 10 hours to remove crystallization water, and Li$_2$CO$_3$ dry at 153 K for 24 hours in ceramic-based crucibles. The components were then finely weighed in stoichiometric proportions to give Li$_7$La$_3$Zr$_2$O$_{12}$ with 4,6,8,10 wt % extra Li (to compensate for the li loss under high temperature and long sintering time) and balled mixing for 6 hours at a speed of 250mp/min. After full mixed, the raw powder was calcined at different temperature in order to get the pure cubic LLZO powder. After calcination, granulation of pure cubic LLZO powder was investigated in the purpose of improving the density of the final pellet. Weighed an appropriate amount of polyvinyl alcohol (87-89% hydrolyzed, Alfa) slowly added into an appropriate amount of distilled water on the magnetic stirring platform to prepare the solution of polyvinyl alcohol with a concentration of 5 wt%. After it fully dispersed, heated it up to accelerate the dissolution. Then adding calcination pure cubic powder into the mortar, slowly add the PVA solution with a mass fraction of 5wt%, make it fully grind. The granulated powder was uni-axially pressed into pellets (10mm diameter, 2mm thickness) and went through isostatic pressing with 220 MPa. These pellets were sintered in alumina crucible with mother powder buried it at the temperature of 1200 °C for 24 h. All the specimens are sintered with a speed of 2°C/min above 1000°C during heating period.
Figure 1. Schematic illustration of the solid phase procedures to fabricate the cubic LLZO.

The surface of each sample was polished to minimize the effect of the roughness on subsequent testing and measurements. Silver was pasted on to the two sides of each sample to serve as electrodes and silver wires were adhered on the electrodes.

2.2. Characterization

The phase of the samples was analyzed by X-ray diffraction (Rigaku, Akishima-Shi, Japan; using Cu Ka radiation of 0.15418 nm) on the range of 10-70 ° with the step speed of 6 °/min. The morphology of the LLZO powders and pellets were observed by scanning electron microscopy (TESCAN, MIRA3). Density of the pellet was calculated by the electronic densimeter (SD-200L) by archimedean drainage. Electrochemical measurements on symmetrical silver Ag/LLZO/Ag cells were carried out using AC electrochemical impedance spectroscopy (EIS, Solartron 1260, UK). The diameter and thickness of sintered samples were measured with vernier caliper, the two surfaces are coated with silver paste to adhere to the silver thread and sintered at 500 degrees for 1 hour to volatile organic solvent. Measurements were performed in static air between 300°C to 500°C, with a 100 mV signal amplitude at open circuit voltage, in the frequency range of 0.1-8×10⁶ Hz. The conductivity, $\sigma$, of the pellet was calculated from the resistance (R) measured at various temperatures using the following relationship:

$$\sigma = \frac{l}{RS}$$

where $L$ is the distance between the two Ag electrodes, $S$ is the surface areas of the measured pellets.

3. Results and discussion

Figure 2 shows the XRD patterns of the synthesized LLZO powders. La$_2$Zr$_2$O$_7$ impurities existed at a low temperature of 800°C, which indicated this temperature is not enough to LLZO phase formation, as showed in the Figure 2(a). The phase is obtained by solid state reactions:

$$\text{Li}_2\text{CO}_3 + \text{La}_2\text{O}_3 + 2\text{ZrO}_2 \rightarrow \text{Li}_2\text{O} + \text{La}_2\text{Zr}_2\text{O}_7 + \text{CO}_2$$

$$7\text{Li}_2\text{CO}_3 + 3\text{La}_2\text{O}_3 + 4\text{ZrO}_2 \rightarrow 2\text{Li}_2\text{La}_2\text{Zr}_2\text{O}_{12} + 7\text{CO}_2$$

When the temperature is low, Li$_2$O and La$_2$Zr$_2$O$_7$ formed, as equation (2). Li$_2$O reacted with the La$_2$Zr$_2$O$_7$ when the temperature increased, as equation (3). As the temperature increased to 900°C,
LLZO formed in the form of both tetragonal and cubic phases. It is interesting to note that the portion of the cubic phase increased with a higher temperature. Little tetragonal phase was found when the temperature reached 950 °C, indicating this temperature is suitable to obtain high pure cubic phase. This result also conformed to the literature, tetragonal phase existed at a moderate temperature [20]. The different Li excess LLZO powder are found to be have slightly difference, but obey same rule with increase of temperature. From comparing the different Li excess in the calcination process, as showed in Figure 2(b), the 4wt% Li excess showed the best percentage of cubic LLZO, indicating 4wt% Li excess is sufficient to compensate for the Li loss in the calcination powder process, extra increase of Li can yield tetragonal phase of LLZO. It is accord with the literature, that only single phase cubic LLZO exists when the atom Li at the range of 5.63 to 6.24 moles [12]. As the Li content is further increased, a transformation from cubic to tetragonal phase appeared. Therefore, we choose the calcination condition that 4wt% excess Li, 950°C of calcination temperature, for 10h,5°C /min of heating rate, as standard to further get the targeted high relative density and conductivity LLZO pellets.

![Figure 2. XRD patterns of calcination powder (a) different temperature, same Li excess concentration, (b) different Li excess concentration, same temperature.](image-url)

![Figure 3. SEM images of the powders (a) calcination at 800°C (b) calcination at 950°C (c,d) granulation after calcination at 950°C.](image-url)
The morphology of the calcination powders at different manufacturing process were observed by SEM, as shown in Figure 3. All powders exhibited particle agglomeration after calcination. The particle size of low temperature calcination (800°C) powder is among the range of 20-40 µm, as shown in the Figure 3 (a). Powders calcination at 950°C illustrated particle size at the range of 80-100 µm, as shown in the Figure 3(b), which is larger than that of low calcination temperature powder (800°C). This is because grain growth faster in higher temperature. Both low and high calcination powder exhibited irregular shape of particles. However, the granulation powder demonstrated uniformly distributed nearly sphere shape of particles, as shown in the Figure 3 (c). The granulation powder was further observed at high magnification, illustrating granulation particle sizes were about 10 µm, as shown in the Figure 3 (d). The morphology indicated that granulation can improve particle size and shape. The small particle size and sphere shape obviously conformed that granulation enhanced the performance of powders during high sintering temperature. The good fluidity of sphere and small powder, can better diffuse in the bulk of pellet and inhibit large pores generated during high temperature sintering [22].

The influence of dwelling time and powder treatment technology on the phase of LLZO pellets was investigated, as shown in the Figure 4. All pellets were sintering at 1200°C for different holding time, with the heating rate of 2°C/min to make sure the complete cubic phase formation. To compensate for the Li loss at this long duration time, high temperature process, mother powder buried sintering process was applied. As for the pellet that powder was granulated, a pre-heated at 600°C for one hour was applied in the purpose of breaking down the organic matter that the granulation process induced. Then followed the same sintering procedure with other pellets. The Figure 4(a) illustrated duration time of 9 h, 18 h, 24 h and 36 h had influence on the final phase formation. With a duration time of 9 h at 1200°C, cubic LLZO phase and Li2ZrO3 with a PDF card #33-0843 co-existed. Extended duration time to 18 h made no difference on the final formation phase, Li2ZrO3 impurities still appeared under this condition. Further increased duration time of 24 h and 36 h were applied for the sintering process. With a duration time of 24 h at 1200°C, only pure cubic LLZO phase existed. Duration time of 9 h, 18 h, and 36 h resulted the exist of both cubic LLZO phase and Li2ZrO3 impurities. This illustrated an appropriate dwelling time is necessary for the final pure cubic phase, at the value of duration time of 24 h. This consequence indicated Li2ZrO3 is a preferred phase for short holding time of 9 or 18 h, and long duration time of 36 h in high temperature. To avoid Li2ZrO3 impurities, sintering process of 1200°C for 24 h was applied for our final desired pellet. Figure 4(b) exhibited both pellets (granulation and non-granulation pellets) exhibited cubic phase sintered at 1200°C for 24 h, suggested granulation of the calcination powder is a feasible method to enhance the sintering performance of particles at high temperature, and doesn’t change the final phase of pellets.

Figure 4. XRD patterns of sintering pellets (a) different duration time, (b) comparison the granulation and non-granulation sintering phase of LLZO pellets.
Figure 5. SEM images of LLZO pellets, (a,b) sintering from non-granulation powder (c,d) sintering from granulation powder.

Scanning electron microscopy (SEM) images of non-granulation and granulation LLZO pellets sintered at temperatures of 1200°C, 24h were displayed in Figure 4 a–d. Without granulation, the pellet had a large amount of dense cavities distributed at the surface, as shown in the Figure 5(a),(b). This is in line with our assumptions that Li loss under high temperature, long dwelling time, indicating the pellet wasn’t dense under this process condition. However, with granulation process, the porosity was significantly reduced and a dense, solid bulk morphology was observed, as illustrated in Figure 5(c),(d). This demonstrated granulation can improve the microstructure through decrease the porosity due to sphere powder has good quality of liquidity and certain grain gradation. Compact stacking can be achieved when pressed it into pellets, and tight bonding can be fulfilled under high temperature sintering.

Besides microstructure, density is another important parameter to characterize the performance of LLZO pellet, high relative density means compact morphology that yields little porosity and grain boundary. Therefore, the conductivity and air stability can be improved. The electronic densimeter analyzed pellets’ density as below, and we calculated their respective relative density. This result is consistent with our assumption that granulation can enhance the performance of powders and decrease pores and grain boundaries of the solid pellets.

Table 1. The actual density and relative density of three different treated LLZO pellets

| Number  | The theory density | The actual density | relative density |
|---------|-------------------|--------------------|-----------------|
| LLZO-1  | 5.131             | 4.112              | 80.13%          |
| LLZO-3  | 5.131             | 4.971              | 96.88%          |

The samples that calcinated from 50-250°C were used for the electrical test and measured their electrical parameters by impedance spectroscopy. Figure 6 shows the Arrhenius plot of the LLZO pellets. The conductivity of specimen at any temperature in the regime examined can also be calculated from the curve. The activation energy was calculated from equation,

\[
\ln \sigma = \ln A - \frac{E_a}{k_B T}
\]
where $E_a$, $A$ and $k_B$ are the activation energy, pre-exponential factor and Boltzmann constant, respectively. The equivalent circuits of $R_b(R_{gb}Q_{gb})$ have been employed here to fit the experimental data. In which, $R_b$ donates the bulk resistance, $R_{gb}$ donates the grain-grain boundary resistance, and $Q_{gb}$ the constant phase element contributions of the grain-grain boundary. In the pellets, both bulk and grain-boundary regions have contributions to the total conductivity. In the view of impedance, $R_t = R_b + R_{gb}$. Figure 6 showed $\ln(\sigma T)$ vs $1/T$ plots for the LLZO solid electrolyte and as shown, a good linear relationship between $\ln(\sigma T)$ vers $1000/T$ was exhibited, thus implying thermal activation of the conductivity. These plots were used to obtain the values of total activation energy ($E_a$) of ionic conduction (from the slope) of these samples. Form calculation, the active energy value of $E_a=0.51\text{eV}$ was obtained, demonstrating its potential application in solid battery devices.

![Figure 6. Arrhenius plot of the LLZO pellets.](image)

4. Conclusions
LLZO was synthesized by solid state reaction using a two-step heat treatment, with a special powder treatment to improve final pellet density. XRD patterns demonstrated that 4% Li excess and 950°C of the calcination temperature were the ideal condition for pure cubic LLZO powder. SEM morphology and electronic densimeter testified granulation process can enhance compact and reduce the pores of the pellets. The synthesized LLZO had a cubic lithium garnet-like structure and a value of active energy value 0.51 ev, which may have some application in solid battery.

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References
[1] Zhao P, Wen W, Cheng J, Cao G, Jin Z, Ming H, Xu Y, and Zhu X 2017 Journal of Power Sources 344 56
[2] Bernstein N, Johannes M D, and Hoang K 2012 Phys Rev Lett 109 205702
[3] Suzuki Y, Kami K, Watanabe K, Watanabe A, Saito N, Ohnishi T, Takada K, Sudo R, and Imanishi N 2015 Solid State Ionics 278 172
[4] Tan J and Tiwari A 2012 Electrochemical and Solid-State Letters 15
[5] Cheng L, Wu C H, Jarry A, Chen W, Ye Y, Zhu J, Kostecki R, Persson K, Guo J, Salmeron M, Chen G, and Doeffer M 2015 ACS Appl Mater Interfaces 7 17649
[6] Jin Y and McGinn P 2011 Journal of Power Sources 196 8683
[7] Kokal I, Somer M, Notten P H L and Hintzen H T 2011 Solid State Ionics 185 42
[8] Xie H, Li Y, and Goodenough J B 2012 Materials Research Bulletin 47 1229
[9] Kumazaki S, Iriyama Y, Kim K H, Murugan R, Tanabe K, Yamamoto K, Hirayama T, and Ogumi Z 2011 Electrochemistry Communications 13, 509
[10] Lee J M, Kim T, Baek S W, Aihara Y, Park Y, Kim Y I, and Doo S G 2014 Solid State Ionics 258 13
[11] Geiger C A, Alekseev E, Lazic B, Fisch M, Armbruster T, Langner R, Fechtelkord M, Kim N, Pettke T, and Weppner W 2011 Inorg Chem 50 1089
[12] Rangasamy E, Wolfenstein J, and Sakamoto J 2012 Solid State Ionics 206 28
[13] Deviannapoorani C, Shankar L S, Ramakumar S, and Murugan R 2016 Ionics 22 1281
[14] Düvel A, Kuhn A, Robben L, Wilkening M, and Heitjans P 2012 The Journal of Physical Chemistry C 116 15192
[15] Li C, Liu Y, He J, and Brinkman K S 2017 Journal of Alloys and Compounds 695 3744
[16] Hanc E, Zajac W, and Molenda J 2014 Solid State Ionics 262 617
[17] Murugan R, Thangadurai V, and Weppner W 2007 Angew Chem Int Ed Engl 46 7778
[18] Xia W, Xu B, Duan H, Guo Y, Kang H, Li H, and Liu H 2016 ACS Appl Mater Interfaces 8 5335
[19] Botros M, Djenadic R, Clemens O, Möller M, and Hahn H 2016 Journal of Power Sources 309 108
[20] David I N, Thompson T, Wolfenstein J, Allen J L, Sakamoto J, and Viyas B 2015 Journal of the American Ceramic Society 98 1209
[21] Baek S W, Lee J M, Kim T K, Song M S, and Park Y 2014 Journal of Power Sources 249 197
[22] Litster J D, Hapgood K P, Michaels J N, Sims A, Roberts M, Kameneni S K, Hsu T 2001 Powder Technology 114 0032