

# Effect of Nb Doping on Phase, Microstructure and Lithium-ion Conductivity of $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ Solid Electrolyte

Di Zhao<sup>1</sup>, Yiwen Yang<sup>1</sup>, Chenglin Zhang<sup>2,\*</sup>, Genxiang Zhu<sup>3,\*</sup>

<sup>1</sup>Institute of Advanced Technology, University of Science and Technology of China, Hefei, Anhui, China.

<sup>2</sup>Anhui Top Additive Manufacturing Technology Co., LTD, Fanchang, Wuhu, Anhui, China.

<sup>3</sup>Hefei Kejing Material Technology Co., LTD, Hefei, Anhui, China.

**How to cite this paper:** Di Zhao, Yiwen Yang, Chenglin Zhang, Genxiang Zhu. (2023) Effect of Nb Doping on Phase, Microstructure and Lithium-ion Conductivity of  $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$  Solid Electrolyte. *Engineering Advances*, 3(2), 84-88. DOI: 10.26855/ea.2023.04.001

**Received:** March 30, 2023

**Accepted:** April 28, 2023

**Published:** June 1, 2023

\***Corresponding author:** Chenglin Zhang, Anhui Top Additive Manufacturing Technology Co., LTD, Fanchang, Wuhu, Anhui, China; Genxiang Zhu, Hefei Kejing Material Technology Co., LTD, Hefei, Anhui, China.

## Abstract

$\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$  (LLZO) solid electrolyte with garnet structure is expected to become an important development direction of lithium-ion batteries in the future due to its large electrochemical window, good heat resistance and high safety. Since the lithium ions in c-LLZO are easier to diffuse than those in t-LLZO, the ionic conductivity of c-LLZO is two orders of magnitude higher than that of t-LLZO. Element doping is an important way to improve its ionic conductivity. Nb doping in LLZO stabilizes the cubic phase structure of LLZO by Zr doping, which will improve the ionic conductivity of LLZO at room temperature. Therefore, in this study, we studied the phase composition, microstructure and room temperature ionic conductivity of LLZO electrolyte doped with different contents of Nb by solid state reaction. Through comparative analysis, the electrolyte prepared by doping Y = 0.4 niobium element content has the best relative density (89.1 %) and room temperature ionic conductivity ( $2.05 \times 10^{-4} \text{S cm}^{-1}$ ).

## Keywords

Solid electrolytes,  $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ ,  $\text{Li}^+$  ionic conductivity

## 1. Introduction

Non-renewable, limited reserves and increasing scale of use have led to an increasingly serious energy crisis on Earth. In order to solve the problem of energy shortage and environmental protection, the development of clean, environmentally friendly, safe, efficient and renewable resources has received great attention and attention worldwide. However, new energy sources such as solar energy and wind energy are intermittent and discontinuous. Therefore, research on efficient energy storage and conversion devices has become an important task for energy development in various countries. High energy density and good cycle performance are the advantages of lithium-ion batteries (LIBs), so lithium-ion batteries stand out from other electrochemical energy storage devices [1].

Highly flammable organic solvents used in commercial lithium-ion batteries are chemically unstable and may cause safety problems (such as thermal runaway, explosion, and combustion) under abuse conditions [2]. Therefore, the development of non-flammable electrolytes is considered to be one of the most effective means to prevent lithium-ion battery safety hazards [3]. Solid-state batteries (SSBs) are considered to be a new generation of devices that overcome the inherent limitations of current lithium batteries and have received extensive attention in recent years. Three main types of solid electrolytes have been developed: solid polymer electrolytes (SPEs), inorganic ceramic electrolytes (ICEs) and solid composite electrolytes (SCEs) [4]. Among many solid electrolytes,  $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$  (LLZO) inorganic ceramic solid electrolyte has attracted much attention due to its high ionic conductivity, good chemical stability and wide electrochemical window. In 2007, Murugan et al. first synthesized  $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$  (LLZO) solid electrolyte [5]. For LLZO, there are two phase structures, namely cubic phase (c-LLZO) and tetragonal phase (t-LLZO) [6]. In the tetragonal phase,

lithium ions are ordered and regularly sorted, and the lithium ion migration distance is longer and the energy required is higher. In the cubic phase, lithium ions are disordered and disorderly sorted, and there are more lithium vacancies, which are easier to migrate and require lower energy. Therefore, the ionic conductivity of tetragonal phase is two orders of magnitude lower than that of cubic phase. Therefore, how to stabilize the cubic phase at room temperature to increase the ionic conductivity of LLZO has become a top priority [7].

In addition to the reasonable preparation method, the doping of LLZO element is also one of the effective ways to obtain a more stable cubic phase structure and improve its ionic conductivity. When other elements are doped into LLZO, not only the framework structure of LLZO changes, but also the concentration of lithium ions can be changed. The change of lithium ion concentration can increase the concentration of lithium vacancies, making lithium ions more disorderly arranged in the lattice, thus stabilizing the structure of the cubic phase and improving the ionic conductivity. Element doping includes doping at Li site, La site and Zr site. Li-site incorporation refers to the addition of high-valent cations in its crystal structure, which increases the content of lithium vacancies and accelerates the conduction of lithium ions in the crystal structure, thereby increasing the ionic conductivity of the solid electrolyte [8]. La-site and Zr-site doping improves the ionic conductivity of the solid electrolyte by changing the bottleneck size of lithium-ion conduction [9].

In this paper, the changes of phase composition, microstructure and room temperature ionic conductivity of LLZO electrolyte doped with different contents of Nb at Zr site were discussed by solid state reaction.

## 2. Experimental Procedures

### 2.1 Synthesis of LLZO powder and ceramics

The experimental materials were high-purity  $\text{LiOH}\cdot\text{H}_2\text{O}$  (purity 98 %, produced by Aladdin),  $\text{La}_2\text{O}_3$  (purity 99.9 %, produced by Aladdin, pre-heated at  $900^\circ\text{C}$  for 12h),  $\text{ZrO}_2$  (purity 99.99 %, produced by Aladdin),  $\text{Nb}_2\text{O}_5$  (purity 99.9 %, produced by Aladdin).  $\text{LiOH}\cdot\text{H}_2\text{O}$ ,  $\text{La}_2\text{O}_3$ ,  $\text{ZrO}_2$  and  $\text{Nb}_2\text{O}_5$  were well weighed according to the stoichiometric ratio of 7-Y:3:2-Y: Y in  $\text{Li}_{7-Y}\text{La}_3\text{Zr}_{2-Y}\text{Nb}_Y\text{O}_{12}$  (Y = 0.2, 0.3, 0.4, 0.5). In order to compensate for the loss of lithium in the high temperature sintering method, we added 10 % lithium hydroxide monohydrate to the raw material.

The measured drugs were poured into the corundum ball mill tank, isopropyl alcohol as solvent, zirconia ball (YSZ) as the ball mill medium, into the tabletop planetary ball mill at  $500\text{ Rmin}^{-1}$  for different times of ball grinding. Then the material after ball grinding is placed in a vacuum oven to dry and remove isopropyl alcohol. The dried powder was put into an alumina crucible and calcined in a Muffle furnace at  $900^\circ\text{C}$  for 6h. Then the pre-sintered powder was ground through a 200-mesh sieve, and 0.5g of the sifted powder was pressed into sheets under different forming methods. Finally, the molded electrolyte blocks were sintered in Muffle furnace at different sintering rates and different sintering times. In the sintering process, in order to reduce the lithium loss, LLZO is used as the master powder to cover the pellet. The master powder will provide lithium or prevent the loss of lithium in the solid electrolyte pellet during the sintering process.

### 2.2 Material characterizations

The phase structure of the LLZO samples were characterized by X-ray diffraction with  $\text{Cu K}\alpha$  radiation over the range of  $10 \sim 60^\circ (2\theta)$ . The microstructure of the LLZO pellets was observed by scanning electron microscopy (ZEISS, Germany). The  $\text{Li}^+$  ionic conductivity was measured using an electrochemistry impedance spectrometer (Donghua Test Technology Co., LTD, China) in the frequency range from 10 MHz to 0.1 Hz at elevated temperature range of  $20\text{-}80^\circ\text{C}$  with 10 mV perturbation amplitude. Au was sputtered on both sides of the sample as blocking electrodes. Impedances were determined from the intercepts of the relevant capacitive arcs at the real axes in the Nyquist plots and conductivities were calculated using the following equation:

$$\sigma = L/(SR) \quad (1)$$

where  $\sigma$  is the ionic conductivity, R is the impedance, L is the pellet thickness, and S is the pellet effective cross-sectional area. Typical dimensions of the pellets were about 1 mm in thickness, 11 mm in diameter.

## 3. Results and Discussion

Fig.1 is the XRD pattern of Nb-LLZO materials with different Nb content. From the diagram, it can be found that the diffraction peaks of Nb-LLZO electrolyte materials prepared with Nb doping amount Y = 0.2, Y = 0.3, Y = 0.4 and Y = 0.5 correspond to the standard card (PDF # 45-0109). When the doping amount of niobium element is Y = 0.2, the diffraction peaks have obvious splitting peaks at  $2\theta = 31.0033^\circ$ ,  $34.0484^\circ$ ,  $38.2139^\circ$  and  $53.1314^\circ$ , indicating that the Nb-LLZO material when Y= 0.2 is not a uniform cubic phase structure but a tetragonal phase and a cubic phase. With the increase of niobium doping amount, the symmetry of the diffraction peaks of the electrolyte materials increases. When the doping amount increases to Y= 0.4, the diffraction peak diagram not only has good symmetry, but also has a

large peak intensity, indicating that the phase structure of the Nb-LLZO material prepared when the doping amount of Nb is  $Y = 0.4$  is a single stable cubic phase structure. However, when the doping amount of Nb element continues to increase, the symmetry of the diffraction peaks at  $2\theta = 56.143^\circ$  and  $57.123^\circ$  begins to decrease, indicating that the crystal structure of Nb-LLZO electrolyte material is no longer a single cubic phase but begins to appear tetragonal phase, indicating that excessive Nb element doping will make the single stable cubic phase structure unstable.

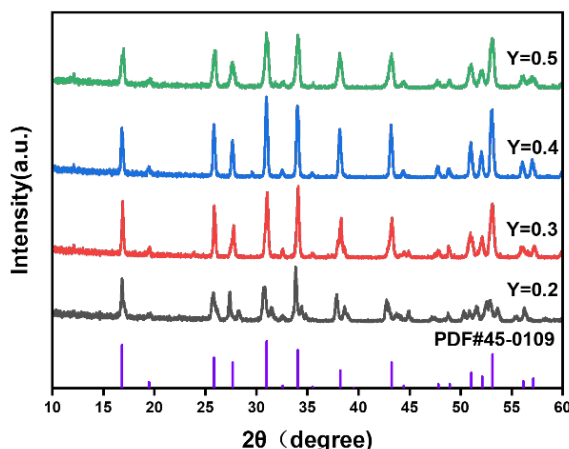


Figure 1. XRD patterns of different Nb element doping.

Fig.2 is the micro-morphology of Nb-LLZO electrolyte materials prepared by doping different contents of Nb. It can be seen from Fig.2 that the density of Nb-LLZO materials increases with the increase of Nb content. When the doping amount  $Y = 0.2$  and  $0.3$ , there are more voids between the material particles. With the increasing amount of niobium doping, the size of the material particles increases, the gap between the particles decreases, the contact between the particles becomes smoother, the 'melting' phenomenon begins to occur between the particles, the grain boundaries are significantly reduced, and the surface of the material gradually becomes smooth and flat, which makes the density of the Nb-LLZO material increase. The reason is that the doped niobium element plays the role of sintering aid in the sintering process, which can make the particles of the material interconnected and the gap between the particles smaller during the sintering process, thereby improving the density of the electrolyte.

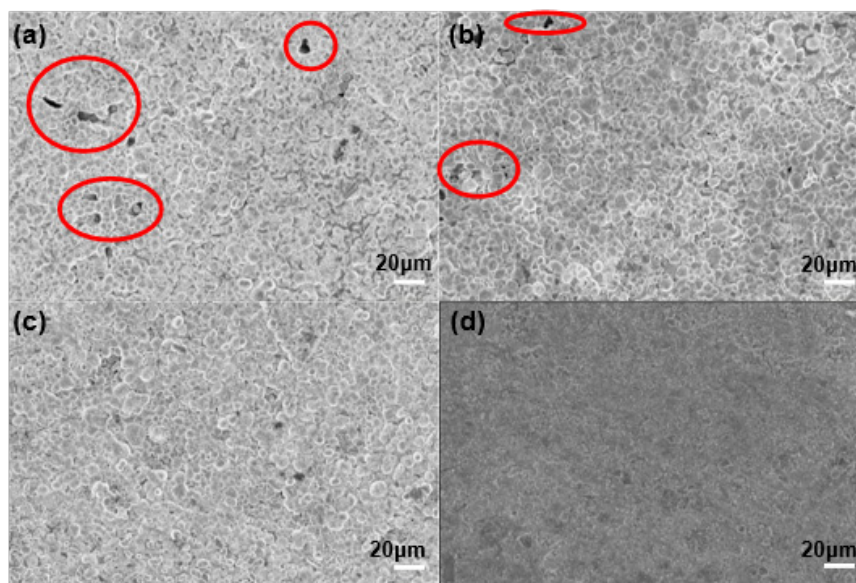


Figure 2. SEM images of different Nb element doping.

Fig.3 is an electrochemical impedance test diagram to study the effect of different contents of Nb doping on the ionic conductivity of Nb-LLZO materials at room temperature. Fig.4 is the trend curve of the density and ionic conductivity of Nb-LLZO electrolyte material at room temperature with the change of doping amount after different content of Nb doping. It can be seen from Fig.4 that when the content of Nb is increased from 0.2 to 0.5, the relative density of the

Nb-LLZO electrolyte material will continue to increase due to the increase of the content of Nb, but the room temperature ionic conductivity will show a trend of increasing first and then decreasing. The reason for the increasing relative density of Nb-LLZO material may be due to the role of niobium as a sintering aid in the sintering process of the material. With the increase of niobium content, the gap between the materials becomes smaller and smaller, and the grain boundary between the particles becomes smaller and smaller, thus making the material more dense, which corresponds to the conclusion drawn from the SEM diagram of the material in Figure 2. The first increase in conductivity is due to the gradual transition of the material from a mixed phase of tetragonal and cubic phases to a single and stable cubic phase with the increase of Nb doping content. However, when the amount of Nb doped is too much, the stable single cubic phase structure begins to change to the tetragonal phase again, so the conductivity shows a downward trend. In summary, when the doping amount of niobium  $Y = 0.4$ , the performance of Nb-LLZO material is the best.

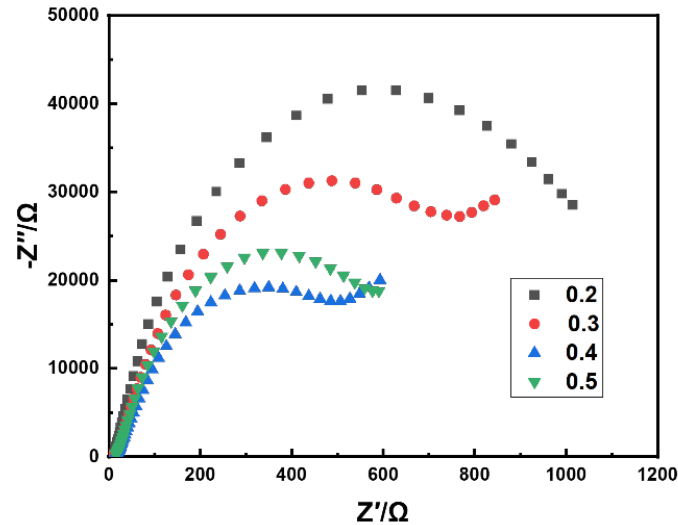


Figure 3. EIS of Nb-LLZO doped with different Nb elements.

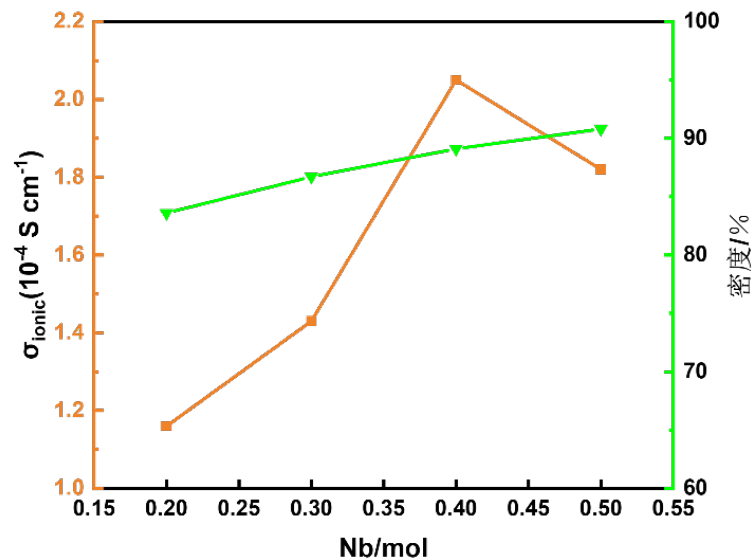
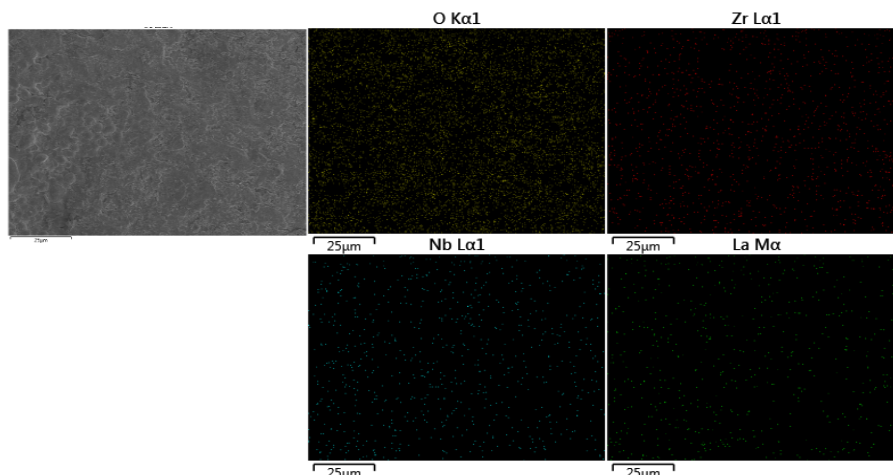


Figure 4. Trends of room temperature ionic conductivity and relative density of Nb-LLZO materials with Nb doping content.

In order to further determine the elemental composition of the Nb-doped LLZO solid electrolyte, the Nb-LLZO solid electrolyte was tested by X-ray energy spectrum, and the test results are shown in Figure 5. It can be seen from the test

diagram that there are four elements of O, La, Zr and Nb in the Nb-LLZO solid electrolyte.



**Figure 5. EDS characterization of Nb-LLZO solid electrolyte.**

#### 4. Conclusion

For LLZO solid electrolyte, element doping can improve its ionic conductivity. In this work, Nb-doped cubic  $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$  solid electrolyte was prepared by solid state reaction. The changes of phase composition, microstructure and room temperature ionic conductivity of LLZO electrolyte with different contents of Nb were studied. Through comparative analysis, the electrolyte prepared by doping  $Y=0.4$  niobium element content has the best relative density (89.1 %) and room temperature ionic conductivity ( $2.05 \times 10^{-4} \text{ S cm}^{-1}$ ). It provides technical support and reference for the further application of garnet solid electrolyte in high energy density solid state batteries.

#### References

- [1] Cao, Shiyu, et al. "Modeling, preparation, and elemental doping of  $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$  garnet-type solid electrolytes: A review." *Journal of the Korean Ceramic Society*, 56.2 (2019): 111-129.
- [2] Zhou, Dong, et al. "Polymer electrolytes for lithium-based batteries: advances and prospects." *Chem*, 5.9 (2019): 2326-2352.
- [3] Hu, Yunhuan, et al. "Hybrid Ionogel Electrolytes for Advanced Lithium Secondary Batteries: Developments and Challenges." *Chemistry—An Asian Journal*, (2022): e202200794.
- [4] Zheng, Yun, et al. "A review of composite solid-state electrolytes for lithium batteries: fundamentals, key materials and advanced structures." *Chemical Society Reviews*, 49.23, (2020): 8790-8839.
- [5] Murugan R, Thangadurai V, Weppner W. Fast lithium ion conduction in garnet-type  $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$  [J]. *Angewandte Chemie International Edition*, 2007, 46(41): 7778-7781.
- [6] Geiger C A, Alekseev E, Lazic B, et al. Crystal chemistry and stability of " $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ " garnet: a fast lithium-ion conductor [J]. *Inorganic chemistry*, 2011, 50(3): 1089-1097.
- [7] Awaka J, Kijima N, Hayakawa H, et al. Synthesis and structure analysis of tetragonal  $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$  with the garnet-related type structure [J]. *Journal of solid state chemistry*, 2009, 182(8): 2046-2052.
- [8] Zhuang, Libin, et al. "Phase transformation and grain-boundary segregation in Al-Doped  $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$  ceramics." *Ceramics International*, 47.16 (2021): 22768-22775.
- [9] Guo, Sijie, Yonggang Sun, and Anmin Cao. "Garnet-type solid-state electrolyte  $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ : crystal structure, element doping and interface strategies for solid-state Lithium batteries." *Chemical Research in Chinese Universities*, 36.3 (2020): 329-342.