Preparation, Microstructure and Electrical Conductivity of LATP/LB Glass Ceramic Solid Electrolytes

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Abstract. The Li2O-Al2O3-TiO2-P2O5 system glass ceramic solid electrolytes were prepared by adding Li3BO3 (LB) frits. The phase composition, microstructure and electrical properties of glass ceramics were investigated by using X-ray diffraction, scanning electron microscopy and AC impedance spectroscopy. The results show that the principal crystalline phase of all glass ceramic samples was LiTi2(PO4)3. The grain sizes of glass ceramic sample increase with the increase of sintering temperature. When the additive amount of LB is 1wt %, the glass ceramic solid electrolyte sintered at 950 °C shows the highest room-temperature ionic conductivity of 1.9×10−4 S.cm−1, which can be expected to be used in solid-state lithium-ion batteries.

Keywords. Glass ceramics; ionic conductivity; solid electrolyte.

1. Introduction
Among various chemical power sources, lithium-ion battery, with its excellent cycle stability, high specific capacity and high energy density, has become the focus of researchers [1-2]. However, the hazard of high-energy lithium-ion batteries is increasingly emerging. At present, the electrolyte of conventional commercial lithium-ion battery is organic liquid electrolyte, which has the disadvantages of leakage of electrolyte, volatilization of harmful substances, flammability, difficulty in effectively preventing lithium dendrite growth, and resulting in explosion and combustion of batteries. In addition, the existence of highly active lithium metal electrode causes the restriction to the service life of the battery by liquid electrode [3].

Compared to traditional organic liquid electrolyte, solid electrolyte has higher safety and conductivity. All-solid-state lithium-ion batteries have a longer cycle life, higher safety and lower requirements for packaging and charge state monitoring circuits [4]. Solid electrolyte is the key component of all-solid-state lithium battery, which generally has the characteristics of high ionic conductivity, small electronic conductivity, wide voltage window, chemical compatibility with electrodes, relative simplicity, low-cost, and batch manufacturing [5].

Lithium-ion conductive solid electrolytes are divided into two categories: inorganic ceramic electrolytes (ICEs), including oxides, sulfides and nitrides, and solid polymer-based electrolytes (SPE) [6]. Among these electrolytes, NASICON type oxide conductor, has the advantages of high chemical and thermal stability, simple synthesis and inexpensive raw materials [7], which can be used as the research object of the novel solid electrolytes. The NASICON solid electrolyte with the system Li2O-Al2O3-TiO2-P2O5 (LATP) is the most promising material for all-solid-state batteries [8]. The crystal structure is formed by TiO6 octahedron and PO4 tetrahedron sharing an angle, which is a rigid [Ti2(PO4)3] structure, enabling Li+ to migrate and conduct electricity in the three-dimensional tunnel structure [9]. Researchers have been conducting research on LATP solid electrolytes, and its synthesis
methods mainly included solid-phase synthesis, sol-gel method and wet chemical method [10]. D.H. Kothari et al. [11] synthesized Li$_{1.3}$Al$_{0.3}$Ti$_{1.7}$(PO$_4$)$_3$ electrolyte by solid-phase reaction method, and explored the influence of trivalent cation dopant in NASICON ceramic system on its conductivity. A.F.A. Faizal et al. [12] prepared a solid electrolyte of the Li$_2$O-TiO$_2$-P$_2$O$_5$ ternary system by mechanical milling method, and studied the influence of heat and mechanical treatment on conductivity, and found that samples treated at 800°C had the highest conductivity of 8.89×10$^{-5}$ S cm$^{-1}$. X. Liu [13] prepared LTAP electrolyte by using sol-gel method, and the conductivity of the obtained electrolyte had reached 1.899×10$^{-4}$ S cm$^{-1}$. K.M. Kim et al. [14] synthesized LATP based solid electrolyte by using the hydrothermal method, and the optimal conductivity was 2.65×10$^{-4}$ S cm$^{-1}$.

Compared with the NASICON ceramic electrolyte, glass-ceramics have compact microstructure, small grain boundary effect, and good chemical stability. The glass-ceramic process also provides a uniform microstructure, controllable grain size and grain boundaries. The preparation of glass-ceramics requires the preparation of basic glass. However, our preliminary study shows that it is very difficult to obtain the Li$_2$O-TiO$_2$-Al$_2$O$_3$-P$_2$O$_5$ system glass ceramics because the glass is easily broken after heat treatment. Therefore, introducing low melting point Li$_3$BO$_3$ (LB) glass additives is expected to improve sintering properties [15].

In this work, Li$_2$O-Al$_2$O$_3$-TiO$_2$-P$_2$O$_5$/Li$_3$BO$_3$ glass ceramics were prepared by solid-phase sintering method. Effects of different heat treatment condition and LB content on the structure, microstructure and electrical conductivity of glass ceramics were investigated. The conductive mechanism of glass ceramic sample was also explored.

2. Experiment

The Li$_{1.3}$Al$_{0.3}$Ti$_{1.7}$(PO$_4$)$_3$ (LATP) glass with a nominal composition of Li$_{1.3}$Al$_{0.3}$Ti$_{1.7}$(PO$_4$)$_3$ was prepared by melt quenching method with the raw materials of Li$_2$CO$_3$ (AR, ≥98.0%), Al$_2$O$_3$ (AR, ≥98.0%), TiO$_2$ (AR, ≥98.0%), NH$_4$H$_2$PO$_4$ (AR, ≥99.0%). The mixed raw materials using ethanol as the medium were ball milled on a planetary ball mill for 12 hours. After drying, it was put into an alumina crucible, kept at 700°C for two hours, and then melted at 1450°C for 2 hours in a muffle furnace. Then, the glass melt was poured into the water for quenching, and ball-milled into glass powder. Similarly, the Li$_3$BO$_3$ glass powder was achieved with the composition of 50Li$_2$O-50B$_2$O$_3$. In LATP glass powders, 1%, 2% and 3% (mass fraction) of Li$_3$BO$_3$ were added and evenly mixed, respectively, and the resulting mixed powder was pressed under 14MPa to make green bodies with a diameter of 12 mm and a thickness of 2 mm. The green bodies were sintered at 850°C-1000°C for 10 h and finally the glass ceramic block material was obtained. After polished and backed silver processing at 550°C for 2 h, the electrical properties of the glass ceramic materials were tested [16].

An X-ray diffractometer (XRD, Bruker AG, D8-Advance, CuKα, 2θ range of 10°-80°) was used to analyze the phase structure of the glass ceramics. A scanning electron microscope (FESEM, FEI Company, Quanta 450 FEG) was used to observe the micromorphology of the glass ceramics. And the ionic conductivity of the glass ceramics was measured by electrochemical comprehensive tester (Agilent, E499A) with a frequency ranged between 40Hz to 1MHz.

3. Results and Analysis

3.1. Phase Structure Analysis

Figure 1 exhibits the XRD spectrum of the glass ceramics with different LB contents sintered at 950°C. The analysis of the XRD results shows that the principal crystalline phase of all glass ceramics is LiTi$_2$(PO$_4$)$_3$ (PDF card: 35-0754, rhombic crystal structure, the space group R-3c) showing an obvious NASICON structure [17], and there are some impure phases such as AlPO$_4$ (PDF card:11–0500) and TiO$_2$ (PDF card: 87-0810). The contents of the principal crystalline phase LiTi$_2$(PO$_4$)$_3$ increase with the increase of LB content. The incorporation of LB promotes the precipitation of the principal crystalline phase LiTi$_2$(PO$_4$)$_3$, however, also causes the precipitation of AlPO$_4$ and TiO$_2$ impure phases.
Compared with the standard cards, the diffraction peaks of all glass ceramic samples shift to the right, indicating that Ti$^{4+}$ is most likely to be replaced by Al$^{3+}$ in the lattice to form Li$_{1.3}$Al$_{0.3}$Ti$_{1.7}$(PO$_4$)$_3$ solid solution phase, resulting in smaller lattice parameters. Table 1 shows the lattice parameters of the corresponding samples, from which it could be seen that both a and b values are reduced compared to the lattice constants of standard LiTi$_2$(PO$_4$)$_3$ (a=b= 8.513 Å, c= 20.878 Å).

| LB content/% | Temperature/°C | a=b (Å) | C (Å)  |
|--------------|----------------|--------|--------|
| 0            | 950            | 8.50133| 20.83787|
| 1            | 950            | 8.46274| 20.86210|
| 2            | 950            | 8.45548| 20.58690|
| 3            | 950            | 8.49767| 20.78550|
| 1            | 900            | 8.46433| 21.01147|
| 1            | 1000           | 8.47522| 21.03146|

Figure 2 displays the XRD diffraction spectrum of the glass ceramic samples at fixed 1wt% LB at different temperatures. The principal crystalline phase of all the samples is LiTi$_2$(PO$_4$)$_3$. In like manner the diffraction peaks shift to the right and the lattice parameters decrease, indicating that Ti$^{4+}$ is replaced by Al$^{3+}$ in the lattice to form Li$_{1.3}$Al$_{0.3}$Ti$_{1.7}$(PO$_4$)$_3$ phase.

3.2. Microstructure Analysis
The microstructure of LATP/LB glass ceramic samples with xwt% LB were investigated, as shown in figure 3. The grain size is around 1 to 4.5 μm. At 950°C, the grain size of the sample without LB is around 1 μm, which are evenly distributed.
Figure 3. SEM images of glass ceramics samples: (a-d) LATP samples with 0-3% of LB sintered at 950 °C, (e and f) LATP samples with 1% of LB sintered at 900 °C and 1000 °C.

And there are a few residual glass phases in the grain pores. At 950°C, the grain size of the sample with 1% LB content is around 1.25μm, which are relatively evenly distributed. AlPO₄ and TiO₂ impurities may fill the pores, making the crystal phase structure compacted [18]. At 950°C, the grain size of the sample with 2% LB content is around 3.3μm, which has more glass phases. The grain size of the sample with 3% LB content at 950°C is around 3.75μm, which has more grains agglomerated and porous. It can be found that when heated at 950 °C, the grain size gradually increases with the increment of LB content. When heated at 900°C, the sample with 1% of LB has larger pores, the distribution of the grain sizes is uneven, and there are some agglomerations among grains. At 1000°C, the grain size of the sample with 1% of LB is the largest, and there are more impurities and pores.

3.3. Conductivity

In an electrochemical AC impedance test of solid dielectric electrodes, when the current conduction process is controlled by both charge transfer and diffusion, the graph of the impedance complex plane consists of a semicircle in the high-frequency region and a straight line at nearly a 45-degree angle in the low-frequency region. The semicircle in the high-frequency is called capacitance arc, and the phenomenon is "dispersion effect" which is related to the non-uniformity of the electrode surface and the adsorption layer on the electrode surface, and is often characterized by constant phase element (CPE) in the fitting of equivalent circuit. This work utilizes the equivalent circuit shown in figure 4 to fit the impedance diagram, where R₁ is the bulk resistance of the system, R₂ is the equivalent resistance of the interface, CPE₁ is the time constant, and W is the Warburg dispersion impedance.

The intercept between the high-frequency region and the horizontal axis is the bulk resistance (Rb). The semicircle in the low-frequency region is the total resistance (Rt), and the resistance of the sample could be obtained with the abscissa of the turning point of the semicircle and the straight line. It can be seen that glass ceramic sample with 1% of LB at 950°C shows the lowest Rt. Figure 5 (a) shows the impedance spectrum of 1% LB added glass ceramic samples with different temperatures measured at room temperature. Figure 5 (b) shows the impedance spectrum of glass ceramic samples with diverse LB (0, 1, 2, 3) sintered at 950°C at room temperature. It is clear that the glass ceramic sample with 1% of LB sintered at 950°C possesses the lowest Rt value. Table 2 lists the conductivity and activation energy of different samples.
Figure 4 The fitting equivalent circuit used in the experiment.

Figure 5 (a) The impedance spectrum of LATP/LB glass ceramic samples with fixed 1wt% LB at different temperature. (b) the impedance spectrum of LATP/LB glass ceramic samples with different LB sintered at 950°C.

Table 2. Conductivity and activation energy of each sample.

| LB content (wt%) | Temperature/°C | Conductivity/S.cm⁻¹ | Activation energy /eV |
|------------------|----------------|----------------------|-----------------------|
| 0                | 950            | 1.70E-04             | 0.34                  |
| 1                | 950            | 1.92E-04             | 0.32                  |
| 2                | 950            | 1.15E-04             | 0.33                  |
| 3                | 950            | 1.20E-04             | 0.38                  |
| 1                | 850            | 9.61E-05             | 0.33                  |
| 1                | 900            | 1.38E-04             | 0.36                  |
| 1                | 1000           | 1.20E-04             | 0.33                  |

Figure 6(a) displays the Arrhenius diagram of each sample. These curves have good linearity and are consistent with the Arrhenius equation:

\[ \sigma T = A \exp\left(\frac{-E_a}{kT}\right) \]  \hspace{1cm} (1)

where \( A \) is the pre-exponential factor, \( E_a \) is the conducted activation energy, and \( K \) is Boltzmann's constant. The conductivity and \( E_a \) values are also listed in table 2. The analysis has shown that as the temperature increases, the activation energy decreases, which is attributed to the generation of M1 vacancy sites [19]. In the LATP system, the generation of M1 vacancy sites is conducive to the
long-term migration of lithium [20].

Figure 6(b) reveals the relationship between \( x \) and the conductivity and activation energy of LATP/LB samples with \( x \) wt% of LB (\( x = 0, 1, 2, 3 \)). The conductivity increases with the increase of LB up to \( x = 1 \), at which the conductivity reaches the maximum value of \( 1.92 \times 10^{-4} \text{S.cm}^{-1} \) and the activation energy correspondingly decreases to the minimum value of 0.32 eV. When \( x \) continues to increase, the conductivity, on the contrary, decreases and the activation energy increases. At 950°C, the glass ceramic sample with 1% of LB content has the maximum conductivity and minimum activation energy.

![Figure 6](image)

**Figure 6.** (a) The Arrhenius diagram of samples with different LB contents and sintering temperatures. (b) The relationship between \( x \) and the conductivity and activation energy of the sample.

4. Conclusion
LATP/LB glass ceramic solid electrolytes have been prepared by the solid phase method. Adding moderate LB can promote sintering densification. All samples adopt the main crystalline phase of \( \text{LiTi}_2(\text{PO}_4)_3 \), however, some impurity phases of \( \text{AlPO}_4 \) and \( \text{TiO}_2 \) coexists. When sintered 950°C for 10 h, the glass ceramic sample with 1% of LB has the highest conductivity of \( 1.92 \times 10^{-4} \text{S.cm}^{-1} \) and the minimum activation energy of 0.32eV, which indicates that it has certain application prospects for solid state electrolytes.

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