**Low temperature synthesis of Al-doped $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ solid electrolyte by a sol-gel
process**

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Abstract

Al-doped $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ (LLZ) was prepared by a sol-gel process using lithium nitrate, lanthanum nitrate hexahydrate, zirconium propoxide and aluminum tri sec-butoxide as starting materials. Single phase of cubic LLZ was obtained by a heat treatment at 700°C , which is lower than that in the solid state reaction process. The LLZ powders were sintered at 900°C using LiBO_2 or Li_3BO_3 to form composite solid electrolyte. In the composite sintered with LiBO_2 , $\text{La}_2\text{Zr}_2\text{O}_7$ was formed as an impurity phase. On the other hand, in the composite sintered with Li_3BO_3 , single phase of cubic LLZ was obtained. The composite of Al-doped LLZ and Li_3BO_3 sintered at 900°C showed the total electrical conductivity of $1.9 \times 10^{-5} \text{ S cm}^{-1}$, while Al-doped LLZ pellet without additives showed $1.6 \times 10^{-6} \text{ S cm}^{-1}$.

Keywords : $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$, sol-gel method, garnet oxide, liquid phase sintering, solid electrolyte

1. Introduction

All-solid-state lithium ion secondary batteries with inorganic solid electrolytes attract attention due to their high safety, reliability and high energy density. Among many kinds of lithium ion conductive solid electrolytes, sulfides materials are known to exhibit higher ionic conductivity than oxide materials because of higher polarizability of sulfide ion [1-4]. However, oxide materials have advantages such as their chemical stability and handling.

Recently, Murugan et al. have reported that cubic garnet type $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ (LLZ) has high lithium ion conductivity ($\sigma_{\text{total}} > 10^{-4} \text{ S cm}^{-1}$) and chemical stability against lithium metal [5]. Thus, LLZ is a promising electrolyte for all-solid-state lithium ion secondary batteries. However, in the conventional solid state reaction method, tetragonal LLZ with bulk conductivity of $10^{-6} \text{ S cm}^{-1}$ is formed at lower calcination temperatures [6], and in order to obtain the cubic phase, calcination above 1150°C is required. Moreover, to obtain dense sintered body, a sintering temperature at around 1200°C is needed [7]. These high temperatures cause a lithium loss, and to suppress a lithium loss, samples must be covered with mother powders. Thus, low temperature synthesis and sintering of cubic LLZ are desired.

About the control of LLZ formation, Geiger et al. have suggested that Al

contamination from alumina crucible stabilizes cubic phase [8], and Rangasamy et al. and Kotobuki et al. have reported that calcination temperature to obtain cubic phase decrease to 1000°C by the addition of γ -Al₂O₃ [9, 10]. However, this temperature is still too high to prevent lithium loss. To lower the synthesis temperature of cubic LLZ, several groups have reported that the synthesis of LLZ through a sol-gel process, and they found that cubic LLZ was obtained at 700-750°C without Al addition [11-13]. However, the phase transition to tetragonal phase or lithium loss at rather low temperature causes the difficulty in the densification of cubic LLZ.

To lower the sintering temperature, addition of sintering additives that have low melting points and make liquid phases below sintering temperature is known to be effective. The liquid phase promotes the densification and coarsening at low temperature [14, 15]. For example, Aono et al. have reported that NASICON type LiTi₂(PO₄)₃ was sintered well at relatively low temperature by using lithium borate or lithium phosphate as sintering additives [16]. Recently, we have proposed a composite electrolyte of LLZ and amorphous Li₃BO₃ as a novel solid electrolyte with high lithium ion conductivity [17]. However, the effects of kinds and amounts of sintering additives to the properties of the composites have not been clarified.

In this study, cubic LLZ were synthesized through a sol-gel process at temperatures

lower than 1000°C. Al was doped to stabilize cubic phase. For the sintering at lower temperatures and formation of the composite electrolytes, LiBO₂ or Li₃BO₃ was added as sintering additives, and the effects of sintering additives to the properties of the composites were examined.

2. Experimental

2.1. Preparation of LLZ particles

LLZ were prepared by a sol-gel process using LiNO₃ (Wako, Japan), La(NO₃)₃•6H₂O (Wako, Japan), Zr(O-*n*-C₃H₇)₄ (Sigma-Aldrich), Al(O-*sec*-C₄H₉)₃, as the starting materials [17]. CH₃COCH₂COOC₂H₅ (EAcAc) was used as a stabilizing agent for the alkoxides. The mole ratio of LiNO₃ : La(NO₃)₃•6H₂O : Zr(O-*n*-C₃H₇)₄ : Al(O-*sec*-C₄H₉)₃ : EAcAc : ethanol is 7 : 3 : 2 : 0.3 : 1.6 : 50. Firstly, LiNO₃ and La(NO₃)₃•6H₂O were dissolved in ethanol. Separately, Zr(O-*n*-C₃H₇)₄ and Al(O-*sec*-C₄H₉)₃ was reacted with EAcAc. The two solutions were mixed, and the obtained solution was stirred at room temperature for 1 h to form white gel. The gel was dried in isothermal bath at 80°C for 12 h, then successively at 150°C for 5 h. The dry gel was ground well and calcinated at temperatures between 600°C and 900°C for 5 h.

2.2 Sintering of LLZ particles

Al-doped LLZ powders obtained with the heat-treatment at 700°C were ball-milled with zirconia ball for 12 h. The particle size of the milled powder was about 1 μm . Milled powders and $\text{LiBO}_2 \cdot 2\text{H}_2\text{O}$ or Li_3BO_3 were mixed in agate mortar. The molar ratio x of 0 to 1.2, where x is defined as the molar ratio of sintering additives to LLZ, was examined in the present study. Mixed powders were pressed into pellets at a pressure of 200 MPa and sintered at 900°C for 10 h in an alumina crucible.

2.3. Materials characterization

X-ray diffraction (XRD) patterns of LLZ powder or sintered pellets were obtained by X-ray diffractometer (XRD-6000, Shimadzu). A scanning electron microscope (SEM) (JSM-6610A, JEOL) was used for the observation of the particles or fracture surface of sintered pellets. The surface of sintered pellets was polished with sandpapers, and Au was sputter-coated onto the both surfaces of the pellets. AC impedance measurements were performed by an impedance analyzer (SI 1260; Solartron) in frequency range 0.1 Hz to 1 MHz. Porosity was calculated by the pellet density determined from the weight and physical dimensions.

3. Results and discussion

Figure 1 shows XRD patterns of LLZ powder with and without Al, calcinated at temperatures at 600, 700 and 900°C. In the samples without Al, cubic LLZ was formed at 700°C, and a tetragonal phase was obtained with calcination at 900°C. Recently, two different cubic phases have been reported to exist [20, 21]. One is a high temperature-cubic phase which is stabilized by Al doping. The other is low temperature-cubic phase which is obtained by hydration of LLZ such as Li^+/H^+ exchange [21]. Li^+/H^+ exchange causes expansion of lattice [21, 22]. The low temperature-cubic phase has larger lattice parameter than that of Al-doped high temperature-cubic phase sintered at around 1200°C. In the present study, cubic LLZ with lattice parameter of 13.096 Å, which is larger than that of Al-doped high temperature-cubic phase sintered at around 1200°C (12.968 Å [5]), was obtained at around 600°C without Al. To restrict hydration reaction between LLZ and moisture, we conducted calcination of dry gel in Ar atmosphere, and tetragonal phase was obtained at 600°C and 700°C, while the cubic phase was obtained with calcination in air. These results indicate that the cubic LLZ without Al obtained at lower calcination temperature in air was that stabilized by hydration. On the other hand, we confirmed that high temperature-cubic phase was obtained by calcination of Al-doped sample at

temperatures over 700°C in Ar atmosphere. Thus, by Al doping, Al was incorporated into LLZ lattice at lower temperatures and cubic structure was stabilized. In the solid state reaction method, calcination temperature over 1000°C was required to obtain cubic phase even if Al source was added as a starting material [9]. Thus, sol-gel process was effective to obtain cubic LLZ at a lower temperature.

The composites with Al-doped LLZ powders obtained with the heat-treatment at 700°C and LiBO₂ or Li₃BO₃ were prepared. XRD patterns of LLZ sintered with LiBO₂ or Li₃BO₃ at 900°C are shown in Fig. 2. In the composites sintered with LiBO₂, main phase was cubic LLZ. However, La₂Zr₂O₇ was observed as impurity phase, and the peak intensity of La₂Zr₂O₇ was increased with an increase in the amounts of LiBO₂. This indicates that LiBO₂ reacted with LLZ during sintering. On the other hand, in the composites sintered with Li₃BO₃, La₂Zr₂O₇ was not observed. LiBO₂ has B-O-B bond which can be attacked by Li₂O [18]. Therefore, LiBO₂ would extract Li₂O from LLZ during sintering and lithium borate with high lithium ion concentration and La₂Zr₂O₇ would be generated. On the other hand, Li₃BO₃ composes of only BO₃³⁻ unit, indicating that Li₃BO₃ did not react with Li₂O. Thus, Li₃BO₃ did not react with LLZ. The reaction between LLZ and the borate was suppressed by the increase of lithium concentration of borate. The peaks of Li₃BO₃ were also not conformed, indicating that

Li_3BO_3 exists as amorphous phase.

Figure 3 shows cross-sectional SEM images of LLZ pellets sintered at 900°C . The pellet sintered without sintering additives had quite porous structure, indicating that LLZ did not sinter well at 900°C without sintering additives. From EDX analysis of cross-section of the pellet, a trace of Al was detected in LLZ without Al doping after sintered at 900°C (the amount of Al was 0.06 mol per 1 mol LLZ). This indicates that Al contamination to LLZ from Al_2O_3 crucible occurs, even if the sintering temperature is 900°C . However, Rangasamy et al. have reported that at least 0.204 mol Al is required to stabilize the cubic phase [9]. Thus, Al contamination during sintering at 900°C does not affect the crystalline phase. In fact, the tetragonal phase was obtained after the heat treatment at 900°C without Al doping (Fig. 1). The composite pellets sintered with LiBO_2 or Li_3BO_3 ($x=0.68$) had denser structure with larger grain size. Dense structure is obtained because lithium borates formed a liquid phase at a low temperature and promoted rearrangement of LLZ particles and grain growth. Lithium borate is assumed to remain at grain boundary after sintering and contribute to lithium ion conduction between LLZ grains.

Figure 4 shows the complex impedance plot for the composite sintered with Li_3BO_3 ($x=0.68$). The semicircle at high frequency and inclined spike in the low frequency

region were observed. The inclined spike is related to electrode polarization to blocking of the ions at the Au electrode. There are many resistance components in the LLZ-Li₃BO₃ composites such as LLZ bulk, Li₃BO₃ bulk, LLZ/LLZ grain boundary and LLZ/Li₃BO₃ interface. However, it is difficult to separate each resistance components. The total resistance was determined from the real part of impedance Z values at selected frequency, in which Z' goes through a local minimum.

Total ionic conductivity at room temperature and porosity of the pellets sintered at 900°C as a function of additive amounts of sintering additives are shown in Fig. 5. The conductivity of the LLZ pellet sintered without sintering additives was $1.6 \times 10^{-6} \text{ S cm}^{-1}$. Although cubic phase of LLZ was formed, the ionic conductivity was quite lower than the pellets sintered at around 1200°C because of its large porosity. In the composites sintered with LiBO₂, the porosity of the pellets decreased with x, and conductivity reached maximum of $8.1 \times 10^{-6} \text{ S cm}^{-1}$ at x=0.68. In x = 0.81, the ionic conductivity drastically decreased. This must be caused by the increase in the amount of La₂Zr₂O₇ (Fig. 2). In the composites sintered with Li₃BO₃, although the porosity was larger compared to the composites sintered with LiBO₂, the conductivity was higher at any additive amounts than that of the composites with LiBO₂. This must be because La₂Zr₂O₇ was not formed in the composites sintered with Li₃BO₃, and the conductivity

of Li_3BO_3 glass is higher than that of LiBO_2 glass (the conductivities of the lithium ion conducting glasses are known to increase with an increase in concentration of Li^+ ion [19]). In the additive amounts range of $x > 0.68$, the conductivity slightly decreased. Since the conductivity of Li_3BO_3 is considerably lower than that of LLZ, the contribution of Li_3BO_3 to the total conductivity was relatively larger. Maximum conductivity was $1.9 \times 10^{-5} \text{ S cm}^{-1}$ at $x = 0.68$. This conductivity is about one order of magnitude lower than that of the pellet sintered at around 1200°C , because of large porosity ($> 22\%$). Nevertheless, lithium borates are found to work effectively as a sintering additive for LLZ.

4. Conclusions

Al-doped $\text{Li}_7\text{La}_3\text{Zr}_2\text{O}_{12}$ (LLZ) was prepared by a sol-gel process. Single phase of cubic LLZ was obtained by a heat treatment at 700°C . By the addition of Al, phase transition to tetragonal phase and decomposition caused by lithium loss were suppressed during sintering at 900°C . The pellets sintered with LiBO_2 or Li_3BO_3 as a sintering additive had denser structure. In the composites sintered with LiBO_2 , the impurity phase of $\text{La}_2\text{Zr}_2\text{O}_7$ was formed. On the other hand, in the composites sintered with Li_3BO_3 , single phase of cubic LLZ was observed. The composites of LLZ and Li_3BO_3 ($x = 0.68$)

sintered at 900°C showed the highest total electrical conductivity of $1.9 \times 10^{-5} \text{ S cm}^{-1}$.

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Figure captions

Figure 1 XRD patterns of LLZ powder with or without Al addition calcined in air.

Figure 2 XRD patterns of LLZ sintered at 900°C with LiBO₂ or Li₃BO₃ .

Figure 3 Cross-sectional SEM images of LLZ pellets sintered at 900°C without sintering additives and with LiBO₂ or Li₃BO₃ (x=0.68).

Figure 4 Complex impedance plot for the composite pellet sintered with Li₃BO₃ (x=0.68).

Figure 5 Ionic conductivity at room temperature and porosity of the pellets sintered at 900°C as a function of additive amount of Li₃BO₃ or LiBO₂.

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5