Preparation of Li$_{1.5}$Al$_{0.5}$Ge$_{1.5}$(PO$_4$)$_3$ solid electrolytes via the co-precipitation method

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ABSTRACT

Li$_{1.5}$Al$_{0.5}$Ge$_{1.5}$(PO$_4$)$_3$ (LAGP) is prepared through co-precipitation and sintered at various temperatures (650 ~ 900°C). Impurity formation is affected by the sintering temperature. Although impurity formation is observed in all the samples, it becomes more prominent at higher sintering temperatures. The crystallinity of LAGP increased with the sintering temperature as evidenced by SEM observations, which show that the edges of the grains become sharper with increases in the sintering temperature. However, the formation of pores is also observed in the pellets sintered at 850°C and 900°C. As a result, the highest Li ion conductivity (7.8 × 10$^{-8}$ S cm$^{-1}$) is obtained when the sintering temperature is 800°C due to the high crystallinity of LAGP and absence of pore formation. This conductivity value is comparable to previously reported values and LAGP synthesis temperature is 400°C lower than required by the melt-quenching method. The co-precipitation method is a promising method for the preparation of LAGP solid electrolytes at low temperatures.

1. Introduction

All-solid-state batteries with nonflammable ceramic electrolytes are expected to solve the safety issues of current commercial Li batteries [1–4]. Na superionic conductor (NASICON)-type oxide-based solid electrolytes [5,6] as well as perovskite-type [7,8] and garnet-type [9,10] solid electrolytes are considered to be promising solid electrolytes due to their reasonably high Li ion conductivity. LATP (Li$_{1+x}$Al$_x$Ti$_{2-x}$(PO$_4$)$_3$) with the NASICON structure which can be formed by partial substitution of Al$^{3+}$ for Ti$^{4+}$ in Li$_2$Ti$_2$(PO$_4$)$_3$ exhibits especially high Li ion conductivity in the order of ∼10$^{-3}$ S cm$^{-1}$ at room temperature [11,12]. We have investigated the preparation of LATP solid electrolytes using the co-precipitation method. Co-precipitation can be defined as simultaneous precipitation of a normally soluble component with a macro-component from the same solution by the formation of mixed crystals through adsorption and occlusion of mechanical entrapment [13]. We found that the sintering temperature could be reduced by 150°C using the co-precipitation method and that PO$_4$ sources largely influenced the properties of LATP [14–16].

It is also well known, however, that LATP-based materials react with Li metal at around 2.5 V vs. Li$^+$/Li due to Ti$^{4+}$/Ti$^{3+}$ reduction [17], restricting the selection of negative electrodes for all-solid-state batteries with the LATP solid electrolyte. In the same NASICON group, Li$_{1.5}$Al$_{0.5}$Ge$_{1.5}$(PO$_4$)$_3$ (LAGP) has a wider electrochemical window because Ge$^{4+}$ is more difficult to reduce than Ti$^{4+}$. LAGP also possesses a high Li ion conductivity of 3.38 × 10$^{-4}$ S cm$^{-1}$ [18]. So far, LAGP solid electrolytes have been prepared using the melt-quenching [19–22], solid-state reaction [23,24], and sol-gel [25] methods. The co-precipitation method makes the materials react uniform at the molecular level and offers the advantages of lower polycrystalline-synthesized temperatures and shorter sintering times. These lower synthesized temperatures and shorter sintering times enable a reduction in process costs for LAGP production. The co-precipitation method has not, however, been applied to the preparation of LAGP solid electrolytes, yet.

In this study, the co-precipitation method was applied for the preparation of LAGP solid electrolytes. The LAGP solid electrolyte was successfully prepared through the co-precipitation method, and its conductivity was comparable to the reported values.

2. Experimental

2.1. Sample preparation

LAGP solid electrolyte was prepared by the co-precipitation method. Li$_2$C$_2$O$_4$ and Al(NO$_3$)$_3·9$H$_2$O were dissolved in deionized water and the solution was heated at 80°C. Ten percent excess amount of Li was added to compensate the evaporation of Li during heat treatment. NH$_4$HCO$_3$ solution was dropped into the solution under vigorous stirring to obtain a co-precipitation. After the co-precipitation had dried, it was calcined at 850°C for 3 h in air. The obtained sample was ground and sieved to obtain the desired particle size.
Ge(CH$_3$O)$_4$ and NH$_4$H$_2$PO$_4$ ethanol solution were dropped into the co-precipitation. The mixture was dried at 100°C to remove the solvent. The dried mixture was then heated at 350°C for 2 h. The obtained precursor powder was ground by ball-milling at 650 rpm for 1 h (Pulver Risette 7, Fritsch) with φ0.5 mm Zirconia balls to supply a sintered pellet preparation. The milled powder was pressed into pellets with 20 mm diameters and then sintered at 650 ~ 900°C for 6 h in air. All reagents were purchased from Wako Chemical Co., Ltd., Tokyo, Japan, and used without further purification.

2.2. Characterization

The as-prepared and milled powders and the sintered pellets were subjected to X-ray diffraction (XRD, Rigaku Ultima-IV) measurement using Cu Kα radiation to identify their crystal phases. Scanning electron microscopy (SEM, JEOL, JSM-6300LA) was used to observe the morphologies of the powders and the pellet cross-sections.

The Li ion conductivity was measured by the AC impedance method. Both surfaces of the sintered pellets were polished to obtain flat surfaces and to control their thickness. Prior to measurement, Au was sputtered onto both sides of the pellet to prepare Li blocking electrodes and to ensure electrical contact.

**Figure 1.** XRD patterns of LAGP precursor powders after calcination at 350°C for 2 h (a) before and (b) after ball-milling.

**Figure 2.** SEM images of LAGP precursor powders after calcination at 350°C for 2 h (a) before and (b) after ball-milling.

**Figure 3.** XRD patterns of LAGP pellets prepared by the co-precipitation method sintered at various temperatures (a) 900°C, (b) 850°C, (c) 800°C, (d) 750°C, (e) 700°C, (f) 650°C.
between the pellets and Cu current collectors. The AC impedance data were collected at ±10mV of voltage signals in the frequency range of 100−1 MHz using a chemical impedance meter (HIOKI Chemical Impedance Meter 3352–80). Measurement was performed at 30°C.

3. Results

Figure 1 shows the XRD patterns of as-prepared powders calcined at 350°C for 2 h before and after ball-milling. In both cases, a broad peak was observed at 2θ = 20° to 40° and the absence of any clear diffraction peak due to the amorphous nature of the samples was confirmed. SEM images of as-prepared powders before and after ball-milling are depicted in Figure 2. Before ball-milling, particles with about 500 nm ~ 1 μm were aggregated to form secondary particles whose diameters were about 10 μm. After ball-milling, the particle size was reduced to ~100 nm. The ball-milling process effectively reduced the particle size, leading to easy sintering in the next process.

Ball-milling power was supplied for pellet preparation. Figure 3 displays XRD patterns of LAGP pellets sintered at various temperatures. Compared with the standard peaks of LiGe₂(PO₄)₃ with the rhombohedral NASICON structure (PDF 80–1922), most of the peaks can be assigned to LAGP, however, small impurities were also observed (Figure 4(a−c)). After sintering at 650°C, AlPO₄ formation was confirmed by a shoulder peak at 2θ = 21.77°. This AlPO₄ formation was observed in all the samples. With increases in the sintering temperature, further impurities were formed. After sintering at 700°C, a peak of Li₄Ge₅O₁₂ was confirmed. This peak was also observed in samples sintered at 750°C, however, it disappeared after sintering at 800°C. Peaks attributed to GeO₂ were confirmed with sintering at 750°C and the peaks became more intense with increases in the sintering temperature.

Figure 4. Assignment of the XRD patterns shown in Figure 3. (a) 900°C and 850°C, (b) 800°C and 750°C, (c) 700°C and 650°C.

Figure 5 shows cross-sectional SEM images of LAGP pellets sintered at various temperatures. After sintering at 650°C, the cross-section was composed of round grains fused each other, indicating that the crystallinity of the sample was low. With increases in the sintering temperature, grains with sharp edges appeared, implying that the crystallinity of the sample was enhanced. Small crystallized grains with sharp edges were observed in samples sintered at 700°C. The crystal grain size became larger with sintering at 750°C, however, both large and small grains were observed, implying that non-uniform growth of the crystal grains occurred. Further crystal growth was observed with sintering at 800°C. The grain size became uniform (about 5 μm). With sintering at above 800°C, however, pore formation was observed. Formation of small pores (about 1 μm in diameter) was confirmed for sintering at 850°C. More pores were formed after sintering at 900°C. Small pores (<1 μm) were distributed throughout the whole pellet. On the contrary, pore formation was rarely observed in pellets sintered at below 850°C.

The relative densities of LAGP pellets sintered at various temperatures are tabulated in Table 1. The relative density increased with the sintering temperature up to 800°C due to the enhancement of the
crystallinity of LAGP. With further increases in the sintering temperature, the relative density declined because of pore formation.

The Li ion conductivity of LAGP pellets sintered at various temperatures was measured by the electrochemical impedance method. Complex impedance plots of the samples are depicted in Figure 6. In all the spectra, a semicircle and a tail were observed in the high- and low-frequency ranges, respectively. This characteristic profile of the impedance plot often appears in ceramics that are ion conductive in nature [26,27]. The intercepts of the semicircles in the high- and low-frequency ranges are assigned to the inner crystal (bulk) and total (inner crystal and grain boundary) impedances, respectively. The estimated bulk ($\sigma_b$), grain-boundary ($\sigma_{gb}$) and total ($\sigma_{total}$) conductivity values are tabulated in Table 2 and summarized in Figure 7. Bulk conductivity increased with the sintering temperature, reached the maximum at sintering temperature of 800°C ($1.0 \times 10^{-3}$ S cm$^{-1}$) and then decreased. The same behavior was observed for grain-boundary conductivity. As a result, the highest total conductivity ($7.8 \times 10^{-5}$ S cm$^{-1}$) was obtained in pellets sintered at 800°C.

4. Discussion

The preparation of LAGP solid electrolytes through co-precipitation was studied. The sintering temperature strongly affected Li ion conductivity. Li ion conductivity increased with increases in the sintering temperature and reached its maximum value at sintering temperature of 800°C. Conductivity decreased with further increases in the sintering temperature. The peak of conductivity is thought to be due to the improvement of the crystallinity of LAGP on one end and the formation of pores and impurities on the other. In sintering at 650°C, round crystal grain shapes were observed, and the crystal grains became sharper with increases in the sintering temperature (Figure 5). This evidenced increases in the crystallinity of LAGP with increases in the sintering temperature. Because amorphous LAGP is not Li ion conductive in nature, LAGP pellets with low crystallinity show low Li ion conductivity. Therefore, Li ion conductivities increased with the sintering temperature. The density of the amorphous phase in LAGP is lower than that of the crystal phase. Therefore, the volume of the pellets decreased with crystallization. With low-temperature sintering, the rate of crystallization was slower than that of sintering. On the contrary, rapid crystallization as well as fast shrinkage of the pellets surpassed the sintering rate with the high-temperature sintering, resulting in pore formation. This behavior was observed in the crystallization of melt-quenching LAGP glass [28]. Pore formation was confirmed in LAGP pellets sintered at 850°C and 900°C. Li ions cannot migrate into the pores. Consequently, the Li ion conductivity decreased at high temperatures. Therefore, the highest Li ion conductivity was obtained after sintering at 800°C. Another possible reason for the variations in Li ion conductivity is impurity formation. Impurity formation is thought to be due to deviations from the target composition caused by Li evaporation in high-temperature sintering. Therefore, impurity formation was promoted at high temperatures and LAGP pellets sintered at high temperatures contained more impurities. In fact, impurity formation
was more obvious in pellets sintered at 850°C and 900°C (Figures 3, 4). Impurities are thought to block Li ion migration, resulting in a reduction in Li ion conductivity (increase in resistance). A high concentration of the impurities is therefore another possible reason for the decrease in Li ion conductivity at high sintering temperatures.

The highest bulk and total Li ion conductivity of LAGP prepared through co-precipitation were $1.0 \times 10^{-3}$ and $7.8 \times 10^{-5} \text{ S cm}^{-1}$, respectively, obtained at 800°C. These values are comparable to previously reported values [18]. The conventional melt-quenching method required heating of precursor powders to above 1200°C and in the sol-gel method, the highest Li ion conductivity was obtained with sintering at 850°C in our previous report [25]. The co-precipitation method can reduce the sintering temperature of bulk LAGP solid electrolytes by 400°C and 50°C compared with the melt-quenching and sol-gel methods, respectively.

This study verified that the sintering temperature influences the Li ion conductivity of LAGP solid electrolytes prepared through co-precipitation. It also showed that the co-precipitation method can reduce the sintering temperature compared with that of the conventional melt-quenching and sol-gel methods. The co-precipitation method is thus a good choice for the preparation of LAGP solid electrolytes at low temperatures.

### Table 2. Li ion conductivities at 30°C of LAGP solid electrolyte sintered at various temperatures.

| Temperature (°C) | $\sigma_b$ (S cm$^{-1}$) | $\sigma_{gb}$ (S cm$^{-1}$) | $\sigma_{total}$ (S cm$^{-1}$) |
|------------------|--------------------------|---------------------------|-------------------------------|
| 650              | $3.8 \times 10^{-4}$     | $1.3 \times 10^{-5}$      | $1.2 \times 10^{-5}$          |
| 700              | $4.4 \times 10^{-4}$     | $1.3 \times 10^{-5}$      | $1.2 \times 10^{-5}$          |
| 750              | $7.9 \times 10^{-4}$     | $7.4 \times 10^{-5}$      | $6.8 \times 10^{-5}$          |
| 800              | $1.0 \times 10^{-3}$     | $8.4 \times 10^{-5}$      | $7.8 \times 10^{-5}$          |
| 850              | $5.0 \times 10^{-4}$     | $1.2 \times 10^{-5}$      | $1.2 \times 10^{-5}$          |
| 900              | $4.6 \times 10^{-4}$     | $1.4 \times 10^{-5}$      | $1.4 \times 10^{-5}$          |
5. Summary

LAGP solid electrolytes were prepared through co-precipitation and sintered at various temperatures (650 ~ 900°C). Impurity formation was influenced by the sintering temperature. Impurities were observed in all the samples, but they became more prominent at high sintering temperatures. Cross-sections of morphology of sintered pellets clearly showed increases in crystallinity with increases in the sintering temperature. However, pore formation was also observed in LAGP pellets sintered at 850°C and 900°C. As a result, the highest Li ion conductivity ($7.8 \times 10^{-5}$ S cm$^{-1}$) was obtained when the sintering temperature was 800°C due to the high crystallinity of LAGP and absence of pore formation. This conductivity value was comparable to previously reported values, and the sintering temperature was 400°C and 50°C lower than those required by the melt-quenching and sol-gel methods, respectively. The co-precipitation method is thus a promising method for the preparation of LAGP solid electrolytes at low temperatures.

Disclosure statement

No potential conflict of interest was reported by the authors.

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