Lithium Ion Conductivities of NASICON-type Li$_{1+x}$Al$_x$Ti$_{2-x}$(PO$_4$)$_3$
Solid Electrolytes Prepared from Amorphous Powder
Using a Mechaenochemical Method

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ABSTRACT

Amorphous (a-LATP) powders with various nominal compositions of Li$_{1+x}$Al$_x$Ti$_{2-x}$(PO$_4$)$_3$ ($x = 0, 0.3, 0.35, 0.4, 0.45, 0.5, 0.6$) in the Li$_2$O-Al$_2$O$_3$-TiO$_2$-P$_2$O$_5$ (LATP) system, were prepared directly from a mixture of Li$_2$O, γ-Al$_2$O$_3$, anatase-type TiO$_2$$_x$, and P$_2$O$_5$ as the starting powder, using mechanical milling (MM) at room temperature. Crystalline LATP (c-LATP) powder with a NASICON-type structure was formed by the heat treatment of mechaenochemically prepared a-LATP powder. In addition, heat-treated c-LATP ($x = 0.5, 0.6$) powders included an impurity phase of crystalline Li$_2$TiAlO$_4$. The sintered c-LATP ($x = 0$) pellet without Al$^{3+}$ doping exhibited a low electrical conductivity on the order of 10$^{-7}$ S cm$^{-1}$ at room temperature. The other hand, the sintered Al$^{3+}$-doped c-LATP ($x = 0.3, 0.4, 0.45$, and 0.5) pellets showed high electrical conductivities on the order of 10$^{-4}$ S cm$^{-1}$ at room temperature. The sintered c-LATP ($x = 0.45$) pellet exhibited the highest lithium ion conductivity (2.9 × 10$^{-4}$ S cm$^{-1}$) at 25°C and the lowest activation energy (30 kJ mol$^{-1}$).

Keywords : Lithium Ion Conductivity, Solid Electrolyte, NASICON-type Structure, Mechanical Milling

1. Introduction

Rechargeable lithium-ion batteries are the commercialized power supply of hybrid cars or electric vehicles. Since inflammable organic compounds are used as solvents for electrolytes, an improvement in the safety of the batteries is required. In recent years, all-solid-state lithium secondary batteries have attracted significant attention. Thus, lithium-ion-conducting solid electrolytes, which consist of non-inflammable inorganic compounds, have been studied in the development of safe and high-performance solid-state batteries. The development of solid electrolytes with high lithium ion conductivities and low activation energies is desired. H. Aono et al. reported that NASICON-type LiM$_2$(PO$_4$)$_3$ (M = Ti, Ge)-based ceramics exhibited high lithium ion conductivities over 10$^{-4}$ S cm$^{-1}$ at room temperature.$^{1-4}$ Glass-ceramics in Li$_2$O-Al$_2$O$_3$-TiO$_2$-P$_2$O$_5$ (LATP) systems were reported to exhibit superionic conductivities over 10$^{-3}$ S cm$^{-1}$ at room temperature. In LATP glass-ceramics, LATP glass has been prepared by conventional melt-quenching at temperatures around 1500°C. Subsequently, LATP glass-ceramics containing a crystalline LiTi$_2$(PO$_4$)$_3$-based solid solution and AlPO$_4$ have been obtained by the heat treatment of LATP glass plates.

Recently, lithium-ion conducting sulfide glasses and sulfide glass-ceramics in Li$_2$S-P$_2$S$_5$ have been prepared by the mechanical milling (MM) method.$^{5-8}$ All-solid-state lithium secondary batteries which use these materials as a solid electrolyte have been developed.$^{9-11}$ On the other hand, we reported a solid electrolyte with a glass-ceramic composition of 14Li$_2$O-9Al$_2$O$_3$-3TiO$_2$-3P$_2$O$_5$, prepared directly from a mixture of Li$_2$O, Al$_2$O$_3$, TiO$_2$, and P$_2$O$_5$ as the starting materials using MM at room temperature.$^{12}$ The solid electrolyte materials in the LATP system were obtained by the heat treatment of the mechaenochemically prepared amorphous powder at a temperature greater than the crystallization temperature. Recently, an amorphous powder of Li$_{1+x}$Al$_x$Ti$_{2-x}$(PO$_4$)$_3$ with $x = 0.3$ (a-LATP ($x = 0.3$)) was prepared from a mixture of starting materials using MM at room temperature.$^{13}$ Fine particles with diameters less than 1 µm were confirmed by scanning electron microscope (SEM) observations. A NASICON-type Li$_{1+x}$Al$_x$Ti$_{2-x}$PO$_4$ ($x = 0.3$) (c-LATP ($x = 0.3$)) solid solution was obtained by the heat treatment of a mechanochemically prepared amorphous powder. The crystallization temperature was close to 600°C. The sintered c-LATP ($x = 0.3$) pellet showed a lithium ion conductivity on the order of 10$^{-4}$ S cm$^{-1}$ at room temperature. With the MM method, the synthesis of LATP solid electrolytes with NASICON-type structures is possible at low temperatures. However, the solid-solution region and the compositional dependence of lithium ion conductive solid electrolytes in LATP systems obtained by MM have not been reported. The fabrication of solid electrolyte materials as all-solid-state lithium secondary batteries is expected.

In this study, we prepared mechanically milled amorphous (a-LATP) powders with various compositions of Li$_{1+x}$Al$_x$Ti$_{2-x}$(PO$_4$)$_3$ from a mixture of Li$_2$O, Al$_2$O$_3$, TiO$_2$, and P$_2$O$_5$; as the crystalline starting material using MM at room temperature. Solid electrolytes with crystalline LiTi$_2$(PO$_4$)$_3$-based NASICON-type structures were prepared from the mechanically milled amorphous powder. The compositional dependency of the electrical conductivities of the sintered pellets will be discussed.

2. Experimental

2.1 Preparation of samples

Li$_2$O powder (Stream Chemicals, Inc., > 95% (99.5%-Li)), γ-Al$_2$O$_3$ (Kojundo Chemical Laboratory Co., Ltd., 99.99%), P$_2$O$_5$ (Wako Pure Chemical Industries, Ltd., 97%), and anatase-type TiO$_2$ (Wako Pure Chemical Industries, Ltd., 99.9%) were used as starting materials. MM was carried out on mixtures of the starting materials in various compositions (Li$_{1+x}$Al$_x$Ti$_{2-x}$(PO$_4$)$_3$) using a planetary ball mill (Fritsch, p-7) at a rotation speed of 450 rpm for 20 h at room temperature under a dry Ar atmosphere. Stainless steel pots and zirconia balls were used for the ball milling. The volumes of the
pots and number of balls were 45 mL and 10, respectively. The diameters of the balls were 10 mm. Mechanical milled powders were heat-treated at 850°C for 2 h in air. X-ray diffraction (XRD) measurements (Rigaku, MiniFlex) with CuKα radiation were performed to estimate the crystalline phase before and after the heat treatment of the mechanical milled powders. The experimental conditions were as follows: tube voltage, 30 kV; tube current, 15 mA; scan speed, 2° min⁻¹; diffraction angle, 5°–80°; and sampling width, 0.01°. Differential thermal analysis (DTA) (Rigaku, Thermo plus TG8120) of the powders was performed under air flow from room temperature to 1000°C at a heating rate of 10°C min⁻¹.

2.2 Preparation of sintered pellets and conductivity measurements

Pellet-type samples were obtained by cold-pressing the powders prepared by MM at 75 MPa. The samples were sintered in an alumina crucible at 900°C for 10 h in air. The electrical conductivities of sintered pellets with diameters of 10 mm and thicknesses of 1.5–2.0 cm were measured. Au was sputtered on both sides of the pellets as an electrode. Then, AC impedance measurements of the sintered pellets with VSP-300 (BioLogic) were carried out between 25 and 60°C in air. The frequency range and applied voltage were 0.1 Hz–1 MHz and 10 mV, respectively.

3. Results and Discussions

Figure 1 shows the XRD patterns of the a-LATP (x = 0, 0.3, 0.35, 0.4, 0.45, 0.5, 0.6) powders obtained by MM of the mixture of starting materials. The peaks of the starting materials for all samples disappeared and halo patterns were observed after MM, although peaks due to anatase-type TiO2 and rutile-type TiO2 were observed. Amorphous powders of the Li2O-Al2O3-TiO2-P2O5 system were prepared directly from a mixture of Li2O, γ-Al2O3, TiO2, and P2O5 using the MM technique at room temperature.

Figure 2 shows SEM images of the a-LATP (x = 0, 0.3, 0.4, 0.45, 0.5, 0.6) powders obtained by MM. Fine particles with diameters less than 1 µm were observed in all samples. In addition, the aggregation of the fine particles was confirmed.

Figure 3 shows the DTA curves of the a-LATP (x = 0, 0.3, 0.4, 0.45, 0.5, 0.6) powders obtained by MM treatment. Fine particles with diameters less than 1 µm were observed in all samples. The exothermic onset temperature of the x = 0 sample was ca. 658°C. On the other hand, the exothermic onset temperature, when x = 0.3, dropped remarkably to 575°C. With samples where x was larger than 0.3, the exothermic onset temperatures dropped gradually with the increase in x. Such results may indicate that the
crystallization of amorphous materials was promoted with increased values of \( x \).

Figure 5 shows the XRD patterns of the c-LATP (\( x = 0, 0.3, 0.35, 0.4, 0.45, 0.5, 0.6 \)) powders after heat treatment at 850°C for 2h. Diffraction peaks assigned to \( \text{LiTi}_2\text{(PO}_4\text{)}_3 \) phase with a NASICON-type structure were observed in all samples. In addition, diffraction peaks assigned to \( \text{Li}_5\text{AlO}_4 \) in the patterns of the c-LATP (\( x = 0, 0.3, 0.4, 0.45, 0.5, 0.6 \)) powders were detected. Such results differed from those of glass-ceramics with the composition of \( 14\text{Li}_2\text{O} - 9\text{Al}_2\text{O}_3 - (1-x)\text{AlPO}_4 \). It was suggested that the solid-solubility limit was ca. \( x = 0.45 \) or less for nominal compositions in \( \text{Li}_{1+x}\text{Al}_{2-x}\text{Ti}_2\text{(PO}_4\text{)}_3 \) (PO_4)_3. Therefore, new solid-electrolyte materials were prepared.

Figure 6 shows the SEM images of the fracture surface of sintered c-LATP (\( x = 0, 0.3, 0.4, 0.45, 0.5, 0.6 \)) pellets obtained by sintering pelletized a-LATP samples at 900°C for 10h. Square particles were observed. Such results suggest the crystallization of amorphous powder as shown in Fig. 2. In addition, a concatenation of particles was observed. The sintered c-LATP (\( x = 0.6 \)) pellets markedly facilitated grain growth and sintering. The formation of \( \text{Li}_5\text{AlO}_4 \) might have promoted the sintering.

Figure 7 shows the Nyquist plots of the AC impedance of the c-LATP (\( x = 0.45 \)) pellet obtained by sintering the pelletized a-LATP (\( x = 0.45 \)) sample at 900°C for 10h. The diameters of the semicircles in the Nyquist plots decreased with increased measurement temperatures. Samples with other compositions yielded similar plots. The total resistance (\( R = \text{bulk} (R_b) + \text{grain boundary} (R_g) \)) was determined from the Z' value for the minimum Z'' value of the semicircle. Then, the electrical conductivities (\( \sigma \)) were calculated from the following formula:

\[
\sigma = \frac{1}{R} \frac{L}{S},
\]

where \( L \) and \( S \) are the thickness and cross-sectional area of the sintered pelletized sample, respectively.

Figure 8 shows the Arrhenius plots of the electrical conductivities of sintered c-LATP (\( x = 0, 0.3, 0.4, 0.45, 0.5, 0.6 \)) pellets. The electrical conductivities for all sintered pelletized samples followed an Arrhenius-type equation:

\[
\sigma = \sigma_0 \exp(-E_a/RT),
\]

where \( E_a \) is the activation energy for conduction, \( \sigma_0 \) is the pre-exponential factor, \( R \) is the gas constant, and \( T \) is the absolute temperature.

Figure 9 shows the compositional dependence of the conductivity at 25°C (\( \sigma_{25} \)) and the activation energy for conduction (\( E_a \)), as determined from the Arrhenius plots shown in Fig. 8. The value of \( \sigma_{25} \) increased as \( x \) increased. The value was maximum for the composition of \( x = 0.45 \). When \( x \) increased further, \( \sigma_{25} \) decreased. The decrease in the electric conductivity was likely because crystalline \( \text{Li}_5\text{AlO}_4 \) was included as an impurity phase. The value of \( E_a \) decreased as \( x \) increased. The composition of \( x = 0.45 \) exhibited a minimum value of \( E_a \) and then the value increased as \( x \).
increased further. Values of $Q_{25} = 2.9 \times 10^{-3} \text{ S cm}^{-1}$ and $E_a = 30 \text{ kJ mol}^{-1}$ were observed for the c-LATP ($x = 0.45$) pellet obtained by sintering the a-LATP ($x = 0.45$) sample at 900°C for 10 h. The activation energy of the sintered c-LATP ($x = 0.45$) pellet prepared from amorphous powder obtained by the mechanochemical method was similar or less than that of Li$_{1+x}$Al$_x$Ti$_2-x$(PO$_4$)$_3$ ($x = 0.3$) ceramics obtained by solid reactions. The apparent densities of various sintered c-LATP pellets were calculated from the true density (ca. 3.0 g cm$^{-3}$) of Li$_2$O-Al$_2$O$_3$-TiO$_2$-P$_2$O$_5$ system were directly prepared from a mixture of starting powders by MM at room temperature. c-LATPs with NASICON-type structures were formed by the heat treatment of mechanochemically prepared amorphous powders in air. We concluded that the solid-solubility limit was ca. $x = 0.45$ or less for nominal compositions in Li$_{1+x}$Al$_x$Ti$_2-x$(PO$_4$)$_3$. The nominal compo-

4. Conclusions

Amorphous powders with various LATP compositions in the Li$_2$O-Al$_2$O$_3$-TiO$_2$-P$_2$O$_5$ system were directly prepared from a mixture of starting powders by MM at room temperature. c-LATPs with NASICON-type structures were formed by the heat treatment of mechanochemically prepared amorphous powders in air. We concluded that the solid-solubility limit was ca. $x = 0.45$ or less for nominal compositions in Li$_{1+x}$Al$_x$Ti$_2-x$(PO$_4$)$_3$. The nominal compo-
sitions of $x = 0.5$ and 0.6 contained crystalline Li$_5$AlO$_4$ as an impurity phase. The sintered c-LATP ($x = 0.45$) pellet exhibited the highest lithium ion conductivity ($2.9 \times 10^{-4}$ S m$^{-1}$) at 25°C and the lowest activation energy (30 kJ mol$^{-1}$). NASICON-type Li$_{1+x}$Al$_{1-x}$Ti$_{2-x}$(PO$_4$)$_3$ solid electrolytes prepared from amorphous powders obtained by the mechanochemical method exhibited high lithium ion conductivities. Moreover, powdery and sintered LATP solid electrolytes prepared from amorphous powders by the mechanochemical method are attractive for the assembly of all-solid-state lithium secondary batteries.

References