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Preparation and characterization of lithium ion conducting Li_2S–P_2S_5–GeS_2 glasses and glass-ceramics

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ABSTRACT

Glasses and glass-ceramics in the system Li_2S–P_2S_5–GeS_2 with the following three compositions of $Li_{7+x}P_{3-x}Ge_xS_{11}$, $Li_7P_{3-y}Ge_yS_{11-y/2}$, and $(100-z)(70Li_2S\cdot30P_2S_5)\cdot zGeS_2$, were prepared by using a mechanical milling technique. At the compositions of $Li_{7+x}P_{3-x}Ge_xS_{11}$ and $Li_7P_{3-y}Ge_yS_{11-y/2}$, conductivity decreased monotonically with an increase in x or y. The conductivity decrease was due to the increase of lithium ion concentration around ortho thio-phosphate which led to the precipitation of the $Li_{3.2}P_{0.96}S_4$ crystal. At the composition of $(100-z)(70Li_2S\cdot30P_2S_5)\cdot zGeS_2$, conductivity was enhanced with an increase in z (up to $z=2$), and the glass-ceramic with 2 mol% of GeS_2 showed the highest conductivity of $5.4\pm0.1\times10^{-3}$ S cm^{-1} at room temperature. From the XRD pattern, germanium would not be incorporated into the $Li_7P_3S_{11}$ crystal. One possible reason for the conductivity enhancement is the increase of the crystallinity of $Li_7P_3S_{11}$ crystal.

1. Introduction

High lithium ion conducting solid electrolytes are strongly desired for the application of all-solid-state lithium secondary battery. Many kinds of solid electrolytes were developed so far [1–3]. Sulfide based solid electrolytes have been attracted much attention because of their high conductivity and wide electrochemical window. A superionic crystal is occasionally formed by heat treatment of glass electrolytes and it shows higher conductivity than the mother glasses. Therefore the development of superionic crystal is important for improving cell performance of all-solid-state battery. The superionic $Li_7P_3S_{11}$ crystal was prepared by crystallization of the $70Li_2S\ 30P_2S_5$ (mol%) glass [4,5]. The crystallized glass, which is so-called glass-ceramic, showed high conductivity of 3.2×10^{-3} S cm^{-1} at room temperature [4]. The $Li_7P_3S_{11}$ crystal has not been obtained by conventional solid state reaction and the crystal was only precipitated by crystallization from the glass. The $Li_7P_3S_{11}$ crystal consists of $P_2S_7^{4-}$ unit and PS_4^{3-} unit. Yamane et al. analyzed the $Li_7P_3S_{11}$ crystal structure by using synchrotron X-ray diffraction and Rietvelt analysis [6]. The $Li_7P_3S_{11}$ phase crystallized in a triclinic cell, space group $P-1$, $a=12.5009(3)$ Å, $b=6.03160(17)$ Å, $c=12.5303(3)$ Å, $\alpha=102.845(3)°$, $\beta=113.2024(18)°$, $\gamma=74.467(3)°$.

Conductivity of glass-ceramic depends on the conductivity of precipitated crystal and its crystallinity. Therefore the precipitation of superionic crystal in the glass-ceramic with high crystallinity is important to enhance the conductivity. In order to increase conductivity of the $Li_7P_3S_{11}$ crystal, we have focused on the element substitution in the $Li_7P_3S_{11}$ crystal. Kanno et al. reported that conductivity of the Li_3PS_4 crystal was largely increased by substituting small amount of third component such as SiS_2 and GeS_2 for P_2S_5. These solid solutions are called thio-LISICONs [7–9]. In many thio-LISICONs, the $Li_{3.25}P_{0.75}Ge_{0.25}S_4$ crystal, which was substituted GeS_2 for P_2S_5, showed the highest conductivity of 2.2×10^{-3} S cm^{-1} at room temperature. Enhancement of the conductivity was due to the formation of superionic crystal (thio-LISICON region II crystal). The Li_3PS_4 crystal shows low conductivity of about 10^{-8} S cm^{-1} at room temperature. Conductivity of the Li_3PS_4 crystal was enhanced more than 5 orders of magnitude by incorporating germanium into the Li_3PS_4 crystal. On the other hand, the $Li_7P_3S_{11}$ glass-ceramic shows high conductivity of 3.2×10^{-3} S cm^{-1}. It is expected that further enhancement of the conductivity would be achieved by incorporating germanium into the $Li_7P_3S_{11}$ crystal.

In this study, preparation of the germanium-incorporated $Li_7P_3S_{11}$ crystal was conducted by crystallization of the Li_2S–P_2S_5–GeS_2 glasses. Three types of incorporations on Lines A, B, and C as shown in Fig. 1 were studied. The Line A, $Li_{7+x}P_{3-x}Ge_xS_{11}$, was normal substitution route (substitution of Ge^{4+} and Li^+ for P^{5+}). This incorporation route is the same as that of the thio-LISICON crystal. In addition to the Line A, other incorporation routes of Line B and C were investigated. The lithium ion concentration was fixed in the Line B, $Li_7P_{3-y}Ge_yS_{11-y/2}$. The ratio of lithium to phosphorus was fixed in the Line C, $(100-z)(70Li_2S\cdot30P_2S_5)\cdot zGeS_2$. Effects of the germanium incorporation on the structure and conductivity of the $70Li_2S\cdot30P_2S_5$ ($Li_7P_3S_{11}$) glasses and glass-ceramics were investigated.

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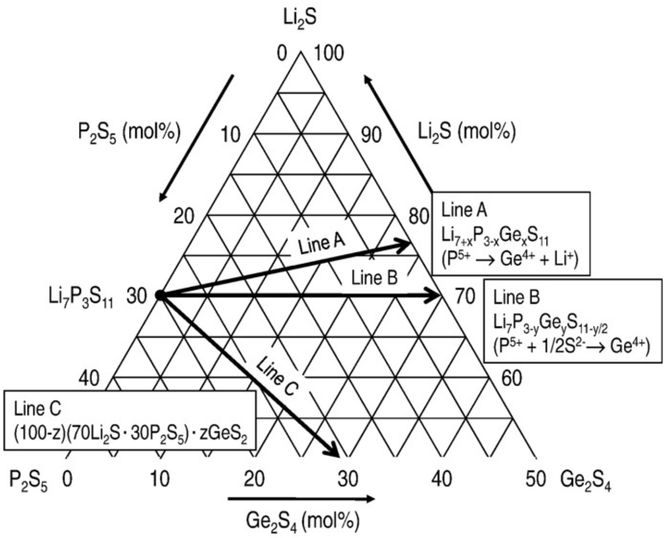

Fig. 1. Target compositions of the $Li_2S–P_2S_5–Ge_2S_4$ system. Compositions of Line A, B, and C are $Li_{7+x}P_{3-x}Ge_xS_{11}$, $Li_7P_{3-y}Ge_yS_{11-y/2}$, and $(100-z)(0.7Li_2S\cdot0.3P_2S_5)\cdot zGeS_2$, respectively.

2. Experimental

The GeS_2 substituted glasses were prepared by the mechanical milling method. Reagent-grade Li_2S (Idemitsu Kosan, 99.9%), P_2S_5 (Aldrich, 99%), and GeS_2 (Fruuchi Chem., 99.999%) powders were used as starting materials. The mixture of these materials was mechanically milled at ambient temperature by a planetary ball mill apparatus (Fritsch Pulverisette 7) using zirconia pot (volume of 45 ml) with 500 zirconia balls (4 mm in diameter). A rotating speed was 510 rpm and the milling time was from 8 to 15 h. The glass-ceramics at all the compositions were prepared by heating the pellets of the obtained glassy powders at 290 °C for 1 h. All the processes were performed in a dry Ar atmosphere.

Raman spectra of the glasses were measured with a Raman spectrophotometer (Jasco NR-1000) using the 514 nm Line of an Ar^+ laser beam. Differential scanning calorimetry (DSC) was performed by using a thermal analyzer (SII, DSC 6200). The heating rate was 10 °C min^{-1}. XRD measurements (CuK_α) were conducted using a diffractometer (Bruker AXS, M18XHF^{22}-SRA). Ionic conductivities were measured for the pelletized samples with 10 mm in diameter and about 1.5 mm in thickness. Carbon paste was applied as electrodes on the both faces of the pellets. Two stainless steel disks coupled with gold wires were attached to the pellets as a current collector. The obtained 2-probe cell was packed in a glass tube and then the tube was sealed with a silicone plug equipped with needle valves, platinum electrodes and a thermocouple. Ac impedance measurements were carried out for the cell using dry Ar gas flow by an impedance analyzer (Solartron, 1260) in the frequency range of 10 Hz to 8 MHz. The temperature range of the measurements was from 25 °C to above the first crystallization temperature of glass samples.

3. Results and discussion

Amorphous samples were obtained by milling at all the compositions studied in this paper. Fig. 2 shows the Raman spectra of the GeS_2-substituted glasses at the compositions: (a) Line A, $Li_{7+x}P_{3-x}Ge_xS_{11}$, (b) Line B, $Li_7P_{3-y}Ge_yS_{11-y/2}$, and (c) Line C, $(100-z)(0.7Li_2S\cdot0.3P_2S_5)\cdot zGeS_2$. The $70Li_2S\cdot30P_2S_5$ (mol%) ($x, y, z=0$) glass consists of $P_2S_7^{4-}$ (407 cm^{-1}) and PS_4^{3-} (420 cm^{-1}) units [10]. At the composition $Li_{7+x}P_{3-x}Ge_xS_{11}$ (Line A), the peak intensity of the PS_4^{3-} unit remains and the peak intensity of the $P_2S_7^{4-}$ unit decreases with increasing germanium content x. Four peaks at 340, 385, 415, and 454 cm^{-1} are observed for the spectra of obtained glasses with large amount of germanium. The peak at 340 cm^{-1} is assigned to the Ge–S–Ge unit with bridging sulfur. The other three peaks at 385, 415, and 454 cm^{-1} are respectively assigned to the $(GeS_{1/2}S_3)^{3-}$, $(GeS_{2/2}S_2)^{2-}$, and $(GeS_{3/2}S)^-$ unit with non-bridging sulfur [11]. These phenomena indicate that the isolated PS_4^{3-} unit is preferentially formed in the glass instead of the $P_2S_7^{4-}$ unit by substitution of GeS_2 for P_2S_5. On the other hand, germanium units with network structure such as $(GeS_{1/2}S_3)^{3-}$ are formed by GeS_2 substitution. At the composition $Li_7P_{3-y}Ge_yS_{11-y/2}$ (Line B), the peak intensity of the $P_2S_7^{4-}$ unit decreases with increasing germanium content y. The change of local structure in Line B is similar to that of the Line A. It is clarified from the spectra in Lines A and B that the substitution of germanium for phosphorus leads to the formation of the phosphorus unit PS_4^{3-} with high lithium ion concentration and germanium units with low lithium ion concentration. We reported that the glass forming reaction was deeply related with the acidity of glass former, and the phosphate component showed higher acidity than the borate and silicate components [12]. It is speculated that the P_2S_5 component is stronger acid

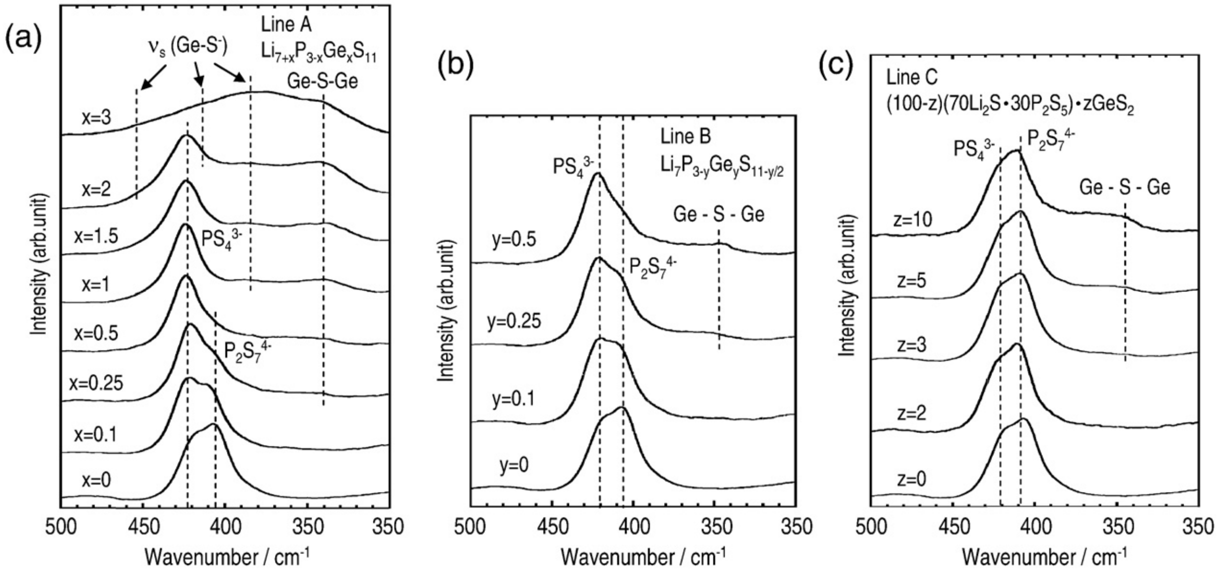

Fig. 2. Raman spectra of the GeS_2-substituted glasses at the compositions of (a) Line A, $Li_{7+x}P_{3-x}Ge_xS_{11}$, (b) Line B, $Li_7P_{3-y}Ge_yS_{11-y/2}$, and (c) Line C, $(100-z)(0.7Li_2S\cdot0.3P_2S_5)\cdot zGeS_2$.