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Structure, ionic conductivity and electrochemical stability of Li_2S–P_2S_5–LiI glass and glass–ceramic electrolytes

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ABSTRACT

The structures, ionic conductivities and electrochemical stabilities of the $(100-x)(0.7Li_2S\cdot0.3P_2S_5)\cdot xLiI$ glass and glass–ceramic electrolytes were investigated. The $(100-x)(0.7Li_2S\cdot0.3P_2S_5)\cdot xLiI$ glasses and glass–ceramics were prepared by mechanical milling in the composition range $0\leq x(mol\%)\leq 20$. All the glasses and glass–ceramics had $P_2S_7^{4-}$ and PS_4^{3-} ions. The $Li_7P_3S_{11}$ crystals were observed in all the glass–ceramics. On the other hand, crystals containing PS_4^{3-} ions were mainly precipitated in the glass–ceramics with increasing the LiI content. The conductivities of glasses increased with increasing the LiI content, and the glass at $x=20$ showed the highest conductivity of 5.6×10^{-4} S cm^{-1}. While the conductivity of glass–ceramics at $x=0$ was 4.2×10^{-3} S cm^{-1}, it decreased sharply with increasing the LiI content. Cyclic voltammetry indicated that the $80(0.7Li_2S\cdot0.3P_2S_5)\cdot20LiI$ glasses exhibited a wide electrochemical stability up to 10 V vs. Li^+/Li.

1. Introduction

Lithium ion batteries are used for electric energy storage. They have flammable liquid electrolytes and thus the safety improvement is required especially for large scale applications. An all-solid-state battery is a candidate for non-flammable batteries and the key material is a solid electrolyte. Sulfide-based glasses and glass–ceramics have been investigated as solid electrolytes because of their high lithium ion conductivities [1–13]. There are several ways to synthesize glasses. Melt quenching is a conventional technique and it needs high temperature to melt samples. Mechanical milling is a technique using a ball mill apparatus and it provides powder glasses at room temperature. Sulfide glasses with high lithium ion conductivities have been synthesized by melt quenching [1–6] and mechanical milling [7–13].

The Li_2S–P_2S_5 system provides a good lithium ion conductor. Li_2S–P_2S_5 glasses and glass–ceramics have the conductivities of 10^{-4} S cm^{-1} and 10^{-3} S cm^{-1}, respectively, at room temperature [7]. The glass–ceramic with the composition of $70Li_2S\cdot30P_2S_5$ (mol%) crystallized from the $70Li_2S\cdot30P_2S_5$ glass has a high conductivity of 4.2×10^{-3} S cm^{-1} and it increased to 5.4×10^{-3} S cm^{-1} by partial substituting P_2S_3 for P_2S_5 [8]. These glass–ceramics have the superionic $Li_7P_3S_{11}$ crystal and it causes high conductivities [7,9].

The addition of LiI to Li_2S–P_2S_5 glasses was studied to increase conductivity for glass electrolytes [4,5]. The lithium ion conductivity of $67Li_2S\cdot33P_2S_5$ glass increased from 10^{-4} S cm^{-1} to 10^{-3} S cm^{-1} by adding 45 mol% LiI [5]. One drawback of the glasses with LiI is their low electrochemical stability; the $67Li_2S\cdot33P_2S_5$ glass was reported to have a electrochemical window of about 2.6 V [5].

In this study, the $70Li_2S\cdot30P_2S_5$ glasses and glass–ceramics containing LiI were synthesized to obtain high lithium ion conductivities. The composition of $70Li_2S\cdot30P_2S_5$ was selected because of its highest lithium ion conductivity. While the Li_2S–P_2S_5 glasses with LiI were prepared by melt quenching in previous reports [4,5], we synthesized the glasses by mechanical milling. The synthesized glasses with LiI were crystallized to prepare glass–ceramics, which have not been reported. The precipitation of $Li_7P_3S_{11}$ based solid solutions is expected to enhance the conductivity of the glass–ceramics. The effects of the LiI addition on conductivity and precipitated crystal in the Li_2S–P_2S_5 glass–ceramics were examined. Electrochemical stability of the $70Li_2S\cdot30P_2S_5$ glasses containing LiI was evaluated by cyclic voltammetry.

2. Experimental

$(100-x)(0.7Li_2S\cdot0.3P_2S_5)\cdot xLiI$ (mol%) ($x=0$, 1, 3, 5, 9, 20) glasses were synthesized by mechanical milling. Regent-grade Li_2S (Idemitsu Kosan, 99%), P_2S_5 (Aldrich, 99%) and LiI (Aldrich 99.99%) were used for starting materials. They were mixed in an agate mortar for 10 min and put into a 45 ml ZrO_2 pot with 500 ZrO_2 balls of 4 mm in diameter. The pot was set in a planetary ball mill apparatus (Fritsch, Pulverisette 7) and mechanical milling was performed at 500 rpm for 10 h. All the processes were carried out in a dry Ar atmosphere.

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Differential thermal analyses (DTA) were performed with a thermal analyzer (Rigaku, Thermo-plus 8120) to observe crystallization temperatures. The milled sample powders were sealed in Al pans in an Ar-filled glove box and heated at 10 °C min^{-1} under N_2 gas flow up to 400 °C. X-ray diffraction (XRD) measurements (CuKα) were performed using a diffractometer (Rigaku, UltimaIV) to identify crystal phases of the milled samples and the heated samples treated above the crystallization temperatures. Raman spectra of the milled samples and the crystallized samples were measured using a Raman spectrometer (Jasco, RMP-210) with 532 nm YAG laser. Ionic conductivities of the milled samples were measured for the pellets with 10 mm in diameter and about 1.5 mm in thickness pressed under 360 MPa. Carbon paste was painted on both faces of the pellets and stainless steel disks were attached to the pellets as current collectors. AC impedance measurements were carried out in a dry Ar atmosphere using an impedance analyzer (Solartron, 1260). The frequency range and the applied voltage were 8 MHz to 10 Hz and 50 mV, respectively. The measurements were conducted from 25 °C to above the first crystallization temperatures. Cyclic voltammetry was carried out for the milled samples at room temperate. The milled samples were pelletized under 360 MPa with 10 mm in diameter. Two-electrode cells were assembled with a stainless steel disk as a working electrode and a lithium metal foil as counter and reference electrodes. The potential was swept between −0.1 and +10 V at scanning rate of 5 mV s^{-1} using a potentiostat (Solartron 1287).

3. Results and discussion

Fig. 1 shows the XRD patterns of the sample powders prepared by mechanical milling. Halo patterns were observed for all the samples. It was suggested that amorphous samples were obtained.

The DTA curves of the milled samples are shown in Fig. 2. Glass transition phenomena were observed between 175 °C and 210 °C, suggesting that the obtained amorphous samples were glasses. The glass transition temperatures (Tg) shifted to lower temperature side with increasing the LiI content. Large exothermic peaks were observed between 220 °C and 270 °C. The samples heated above these temperatures exhibited crystalline XRD patterns as shown in Fig. 3, and thus these exothermic peaks were caused by the crystallization of the glasses. The crystallization temperatures (Tc) also shifted to lower temperature side with increasing the LiI content. It indicates that the addition of LiI to $70Li_2S{\cdot}30P_2S_5$ glasses make it easy to form glass–ceramics at lower temperatures.

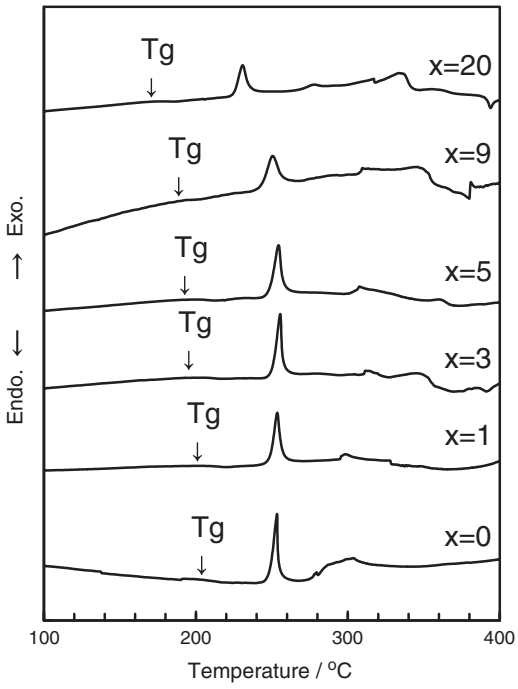

Fig. 2. DTA curves of the $(100-x)(0.7Li_2S{\cdot}0.3P_2S_5){\cdot}xLiI$ samples prepared by mechanical milling.

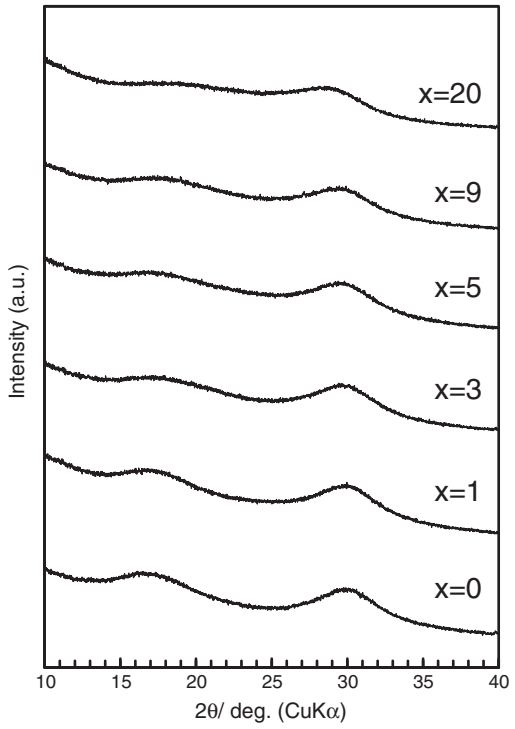

Fig. 1. XRD patterns of the $(100-x)(0.7Li_2S{\cdot}0.3P_2S_5){\cdot}xLiI$ samples prepared by mechanical milling.

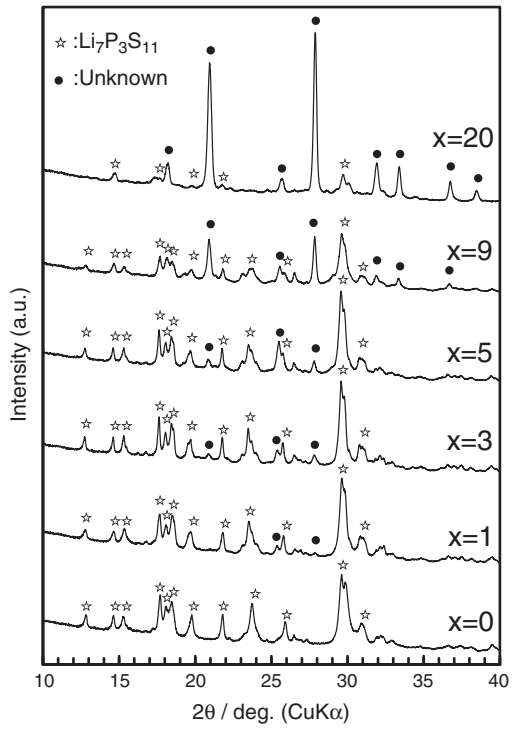

Fig. 3. XRD patterns of the $(100-x)(0.7Li_2S{\cdot}0.3P_2S_5){\cdot}xLiI$ glass–ceramics prepared by heat treatment.