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Synthesis and characterization of Li$_2$S–P$_2$S$_5$ based glass–ceramic electrolytes with lithium halides

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Synthesis and characterization of Li$_2$S–P$_2$S$_5$ based glass–ceramic electrolytes with lithium halides

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1. General introduction

Lithium ion batteries (LIBs) are widely used in portable electronic equipments such as laptop computers and mobile phones [1, 2]. Large capacity LIBs are also produced for electric vehicles and hybrid cars. Household power storage appliances using LIBs are recently commercialized. The large LIBs are expected to be used for power storage at renewable energy sites such as sunlight and wind with the aim of smoothing the power. In addition, LIBs are expected to be utilized in electric power grids with the aim of power storage and load-frequency control [3–5].

LIBs have advantages such as high energy density, high energy efficiency and low self-discharge [1, 4]. High energy density is the most remarkable merit. High energy density makes LIBs compact and has been expanding the use of the battery. High voltage of lithium ion cells causes the high energy density. The voltage of the cells is above 3.5 V, which is three times the voltage of lead acid batteries and nickel hydrogen batteries. Liquid electrolytes containing organic solvents such as ethylene carbonate, diethyl carbonate and dimethyl carbonate are used in LIBs because the organic electrolytes can withstand the voltage of LIBs [6]. However, organic electrolytes bring a risk of burning because of their flammability. Therefore safety devices have to be provided to reduce the burning risk [7–9].

Replacing the flammable electrolytes with non-flammable ones is effective to improve the safety of lithium ion batteries. The conductivity of organic electrolytes is about $10^{-2}$ S cm$^{-1}$ at room temperature [6]. High conductivity comparable to organic electrolytes is required for the non-flammable electrolytes. Two kinds of solid electrolytes have been mainly studied as new electrolytes: polymers and inorganic solids [10]. Above all, inorganic solid electrolyte is a strong
candidate. All-solid-state batteries using inorganic solid electrolytes are expected to improve the safety, reliability and performance of lithium ion batteries [11, 12]. Single-ion conduction of the solid electrolyte reduces side reactions causing degradation of reliability. Non-flammability provides a possibility of low manufacturing costs by simplification of safety devices. High capacity electrode materials suitable for the solid electrolyte are expected to increase the energy density of the batteries. High electrochemical stability of the solid electrolyte makes it possible to fabricate high voltage cells above 5 V. Lamination of solid electrolytes and bipolar electrodes will make battery packages compact.

As lithium ion conductors, oxide crystal, oxide glass-ceramic, sulfide crystal, sulfide glass and sulfide glass-ceramic sometimes have high conductivities at room temperature [10–12]. Crystal electrolytes with high conductivities have structures suitable for ion diffusion. Element substitution is effective to increase the conductivity of crystal electrolytes [13]. Glass electrolytes have large free volume promoting ion diffusion. Introduction of elements with high polarizability and increase of carrier ion concentration is effective to enhance the conductivity of glass electrolytes. Glass-ceramic electrolytes containing metastable crystals are prepared by careful heat treatment for precursor glasses. High ionic conductivity of the precipitated crystal provides glass-ceramic with a remarkable conductivity [11].

Among oxide crystal electrolytes, La$_{2/3-x}$Li$_{3x}$TiO$_3$ with perovskite structure, Li$_7$La$_3$Zr$_2$O$_{12}$ with garnet structure and Li$_{1+x}$Al$_x$Ti$_{2-x}$(PO$_4$)$_3$ with NASICON-type structure have high lithium ion conductivity at room temperature. La$_{0.51}$Li$_{0.34}$TiO$_2$ with perovskite structure has a conductivity of $1.0 \times 10^{-3}$ S cm$^{-1}$ at room temperature [14]. However, selection of active materials is restricted because titanium ions are reduced at around 1.8 V vs. Li$^+$/Li. Li$_7$La$_3$Zr$_2$O$_{12}$ with garnet structure has a conductivity of $3.0 \times 10^{-4}$ S cm$^{-1}$ [15]. This electrolyte has an
electrochemical window of 0–5 V vs. Li+/Li, and therefore lithium metal can be used as an electrode. However, it is necessary to sinter the electrolyte at temperatures higher than 1200 °C. In addition, it is difficult to obtain a single phase crystal. Li$_{1.3}$Al$_{0.3}$Ti$_{1.7}$(PO$_4$)$_3$ with NASICON-type structure has a conductivity of 7.0 × 10$^{-4}$ S cm$^{-1}$ [16]. A weak point of this electrolyte is reduction of titanium ion, the same as La$_{2/3}$–Li$_{3x}$TiO$_3$. As oxide glasses, Li$_2$O–B$_2$O$_3$ glasses have been investigated [17–21]. Li$_2$O–B$_2$O$_3$ oxide glasses have a poor conductivity of 10$^{-7}$ S cm$^{-1}$ at room temperature [17]. The addition of lithium halide to the glass increases the conductivity. The conductivity of the 36Li$_2$O·64B$_2$O$_3$ (mol%) glass is increased by the addition of LiF, LiCl, LiBr and LiI from 10$^{-4}$ S cm$^{-1}$ to the value above 10$^{-3}$ S cm$^{-1}$ at 300 °C [18, 19]. The addition of larger halide ions provides higher ionic conductivity. Higher content of added lithium halide causes higher conductivity. The 24Li$_2$O·41B$_2$O$_3$·35LiCl glass shows a conductivity of 10$^{-2}$ S cm$^{-1}$ at 300 °C and, however, the conductivity at room temperature is 10$^{-6}$ S cm$^{-1}$. The 33Li$_2$O·67B$_2$O$_3$ glass has a conductivity of 1 × 10$^{-4}$ S cm$^{-1}$ at 300 °C [21]. Substitution of Cl$^-$ ions for O$^{2-}$ ions increases the conductivity and the 16Li$_2$O·67B$_2$O$_3$·17LiCl glass shows a conductivity of 1 × 10$^{-3}$ S cm$^{-1}$ at 300 °C. Oxide glass-ceramics in the systems Li$_2$O–Al$_2$O$_3$–TiO$_2$–P$_2$O$_5$ and Li$_2$O–Al$_2$O$_3$–GeO$_2$–P$_2$O$_5$ were investigated. Glass–ceramics of Li$_{1.07}$Al$_{0.69}$Ti$_{1.46}$(PO$_4$)$_3$ and Li$_{1.5}$Al$_{0.5}$Ge$_{1.5}$(PO$_4$)$_3$ have conductivities of 1.3×10$^{-3}$ S cm$^{-1}$ and 4.0 × 10$^{-4}$ S cm$^{-1}$, respectively, at room temperature [22–26]. An important advantage of oxide electrolytes is high stability in the air. It makes easy to handle them. A disadvantage of oxide electrolytes is a large resistance of grain boundary [12]. Powders of oxide electrolytes have to be pressed and sintered to form an electrolyte layer or an electrode layer. The pressed layer of oxide electrolytes has a large resistance because the brittleness of the oxide makes poor contacts between particles. The sintered process sometimes causes involuntary
reactions between electrolytes and active materials [12]. The reactions increase the resistance of electrode layers.

Sulfide crystal of γ-phase Li$_3$PS$_4$ has a poor conductivity of $3 \times 10^{-7}$ S cm$^{-1}$ [27, 28]. However, Li$_{4-x}$Ge$_x$P$_2$S$_4$ and Li$_{4-x}$Si$_x$P$_2$S$_4$ called thio-LISICON crystals have high conductivities [13, 29]. The composition dependence of conductivity was studied in detail. Li$_{3.25}$Ge$_{0.25}$P$_{0.75}$S$_4$ has a conductivity of $2.2 \times 10^{-3}$ S cm$^{-1}$ at room temperature [13]. Recently, new crystal of Li$_{10}$GeP$_2$S$_{12}$ was reported [30]. The crystal shows extremely high conductivity of $1.2 \times 10^{-2}$ S cm$^{-1}$ and wide electrochemical stability up to 5 V vs. Li$^+/Li$. Lithium argyrodites of Li$_6$PS$_3$I, Li$_6$PS$_3$Br and Li$_6$PS$_3$I were synthesized [31, 32]. Li$_6$PS$_3$Cl showed a high conductivity of $1.3 \times 10^{-3}$ S cm$^{-1}$.

Sulfide glass electrolytes containing Li$_2$S are good lithium ion conductors. Glasses at various compositions were synthesized by a melt quenching technique in 1980s. The conductivity of $10^{-6} - 10^{-4}$ S cm$^{-1}$ is obtained in binary systems such as Li$_2$S–P$_2$S$_5$, Li$_2$S–B$_2$S$_3$, Li$_2$S–GeS$_2$ and Li$_2$S–SiS$_2$ [33–43]. The conductivities of the sulfide glasses are increased by the addition of lithium halides, the same as oxide glasses. Glasses with high lithium ion concentration generally have high conductivity and the addition of larger halide ions provides higher conductivity. The 37Li$_2$S·18P$_2$S$_5$·45LiI has a conductivity of $1 \times 10^{-3}$ S cm$^{-1}$ at 25 ºC [34, 35]. The conductivity of the 30Li$_2$S·26B$_2$S$_3$·44LiI is $1.7 \times 10^{-3}$ S cm$^{-1}$ [36]. Although the 40Li$_2$S·60GeS$_2$ glass shows a conductivity of $3 \times 10^{-6}$ S cm$^{-1}$, the 24Li$_2$S·36GeS$_2$·40LiI glass has a higher conductivity of $1.2 \times 10^{-4}$ S cm$^{-1}$ at room temperature [37]. The 50Li$_2$S·50SiS$_2$ glass has a conductivity of $1.2 \times 10^{-4}$ S cm$^{-1}$ at 25 ºC. It increases to $2.7 \times 10^{-4}$ and $3.2 \times 10^{-4}$ S cm$^{-1}$, respectively, in the composition of the 40Li$_2$S·40SiS$_2$·20LiCl and the 35Li$_2$S·35SiS$_2$·30LiBr [38, 39]. The 42Li$_2$S·28SiS$_2$·30LiI glass quenched using a twin-roller apparatus shows a
conductivity of $8.2 \times 10^{-4}$ S cm$^{-1}$ [39, 40]. The conductivity of the $42\text{Li}_2\text{S} \cdot 28\text{SiS}_2 \cdot 30\text{LiI}$ glass increases to $1.8 \times 10^{-3}$ S cm$^{-1}$ by quenching in liquid N$_2$ [43]. However, it was reported that the glasses containing lithium halide had poor electrochemical stabilities [35]. $\text{Li}_2\text{S} \cdot 3\text{SiS}_2 \cdot 3\text{Li}_3\text{PO}_4$ and $\text{Li}_2\text{S} \cdot 3\text{SiS}_2 \cdot 3\text{Li}_4\text{SiO}_4$ glasses without lithium halides were synthesized by twin-roller quenching [44–46]. The conductivities of the $63\text{Li}_2\text{S} \cdot 36\text{SiS}_2 \cdot 1\text{Li}_3\text{PO}_4$ and the $95(0.6\text{Li}_2\text{S} \cdot 0.4\text{SiS}_2) \cdot 5\text{Li}_3\text{SiO}_4$ glasses are $1.5 \times 10^{-3}$ and $2 \times 10^{-3}$ S cm$^{-1}$ at 25 °C respectively. In melt quenching, starting materials enclosed in a quartz glass tube are heated at temperatures above melting point. Then the melt is quenched rapidly by pouring into cold water or liquid N$_2$ and using a twin-roller apparatus to obtain a glass. Glasses also can be synthesized by mechanical milling [47]. In mechanical milling, starting materials are milled using a planetary ball milling apparatus. The milling is performed at room temperature. The glasses synthesized by mechanical milling are homogeneous fine powders, which are easy to use in an all-solid-state battery. It was reported that the glass obtained by mechanical milling had almost the same local structure and conductivity as those of the glass synthesized by melt quenching [48]. Powder sulfide glasses prepared by mechanical milling can be easily pelletized by press-molding.

Sulfide glass-ceramics of $\text{Li}_2\text{S} \cdot 2\text{P}_2\text{S}_5$ system have been studied [48–55]. The $80\text{Li}_2\text{S} \cdot 20\text{P}_2\text{S}_5$ glass-ceramic prepared by heat treatment of the $80\text{Li}_2\text{S} \cdot 20\text{P}_2\text{S}_5$ glass shows a conductivity of $1.3 \times 10^{-3}$ S cm$^{-1}$ [49]. This glass-ceramic has thio-LISICON analog structure showing the same XRD pattern as that of region II in thio-LISICON $\text{Li}_{4-x}\text{Ge}_x\text{P}_2\text{S}_4$. A new crystal of $\text{Li}_7\text{P}_3\text{S}_{11}$ was precipitated in the $70\text{Li}_2\text{S} \cdot 30\text{P}_2\text{S}_5$ glass by heat treatment [49]. This glass-ceramic showed a notable conductivity of $3.2 \times 10^{-3}$ S cm$^{-1}$. The conductivity increased to $5.2 \times 10^{-3}$ S cm$^{-1}$ by changing the heating condition [50]. The crystals of the thio-LISICON analog and
Li$_7$P$_3$S$_{11}$ cannot be obtained by normal solid-state reaction. These crystals change into low conductive phases by an additional heat treatment at high temperatures [49]. Therefore the crystals of the thio-LISICON analog and Li$_7$P$_3$S$_{11}$ are metastable phases precipitated from glass phases by heat treatment. The Li$_7$P$_3$S$_{11}$ crystal is also precipitated by rapid quenching of melt, indicating that the crystal is a high temperature phase [48]. It was reported that the 70Li$_2$S·30P$_2$S$_5$ glass-ceramic added with P$_2$O$_5$ had a high electrochemical stability [51]. The 70Li$_2$S·29P$_2$S$_5$·1P$_2$S$_3$ and the 70Li$_2$S·28P$_2$S$_5$·2GeS$_2$ glass-ceramics have a conductivity of $5.4 \times 10^{-3}$ S cm$^{-1}$ [52, 53]. Sulfide glass-ceramics can be molded as easily as sulfide glass. It is easy to make an electrolyte layer with high conductivity. Sulfide glass-ceramics are highly expected as electrolytes of all-solid-state batteries.

As mentioned above, a lot of lithium ion conductors have been studied. Glasses provide high conductivities in a wide range of composition. Incorporation of lithium halides into glasses is effective to enhance the conductivity. Binary systems of oxide glasses have low conductivity below $10^{-7}$ S cm$^{-1}$. However ternary systems of oxide glasses added with lithium halides show a high conductivity of $10^{-6}$ S cm$^{-1}$. Increase of lithium ions and introduction of halide ions enhance the conductivity. Increase of lithium ion concentration means an increase of charge carriers. The high polarizability of halide ions can be expected to have low ability to attract lithium ions. These two factors enhance the conductivity. The larger the amount of lithium halides is, the higher the conductivity is. The higher the polarizability of the halide ion is, the higher the conductivity is [18]. The conductivity of binary sulfide glasses is also increased by incorporation of lithium halides [38]. Sulfide glasses generally have higher conductivity than oxide glasses because the polarizability of sulfide ions is higher than that of oxide ions. Glass-ceramics show higher conductivity compared to the corresponding glasses in some cases. Precipitation of metastable phases with high lithium ion conductivity
makes the glass-ceramics excellent lithium ion conductors. Binary sulfide
glass-ceramics such as the $80\text{Li}_2\text{S} \cdot 20\text{P}_2\text{S}_5$ and the $70\text{Li}_2\text{S} \cdot 30\text{P}_2\text{S}_5$ have a high conductivity of $10^{-3}$ S cm$^{-1}$. However $\text{Li}_2\text{S} \cdot \text{P}_2\text{S}_5$ glass-ceramics added with lithium halide have not been reported.

In this study, ternary glass-ceramics containing $\text{Li}_2\text{S}$, $\text{P}_2\text{S}_5$ and lithium halide as starting materials were synthesized in the aim of increasing the lithium ion conductivity. The ternary glass-ceramics would have higher conductivity than the binary glass-ceramics because the precursor ternary glasses which remained in the glass-ceramics have high conductivity. If halide anions were introduced into a crystal lattice in glass-ceramics, the conductivity of the crystal would be increased. A new crystal with high conductivity might be precipitated from the precursor ternary glasses. Therefore the ternary glass-ceramics were synthesized, and the conductivities and crystalline phases of the glass-ceramics were examined.

As a way to prepare precursor glasses, mechanical milling was chosen. The reported $\text{Li}_2\text{S} \cdot \text{P}_2\text{S}_5$ glasses added with lithium halide were synthesized by melt quenching requiring high temperatures [34, 35]. In contrast, mechanical milling can be conducted at room temperature. Glasses can be synthesized in only one process of milling. Fine powders available for all-solid-state batteries can be directly obtained. The properties of the ternary glasses synthesized by mechanical milling were also examined.

This doctoral thesis consists of five chapters indicated below:

Chapter 1

This chapter describes background and purpose of this research.

Chapter 2

This chapter describes preparation and characterization of ternary glasses
and glass-ceramics in the systems containing Li₂S, P₂S₅ and LiI. In section 2-3-1, incorporation of LiI into 70Li₂S·30P₂S₅ glass-ceramic was investigated. The effects of the LiI incorporation on conductivity and precipitated crystal in the Li₂S–P₂S₅ glass-ceramics were examined. Electrochemical stability of the 70Li₂S·30P₂S₅ glasses containing LiI was evaluated by cyclic voltammetry. Ternary glasses and glass-ceramics of the 80Li₂S·20P₂S₅ added with LiI were synthesized in section 2-3-1. The crystalline phases and the conductivities of the glass-ceramics were examined.

Chapter 3
In this chapter, LiBr was incorporated into the 70Li₂S·30P₂S₅ glasses and glass-ceramics. The glass-ceramic electrolytes were synthesized by mechanical milling and subsequent heat treatment. The crystalline phases and the conductivities of the glass-ceramics were examined. An all-solid-state cell was fabricated and its charge–discharge performance was investigated.

Chapter 4
Lithium halides of LiF, LiCl, LiBr and LiI were incorporated into the 70Li₂S·30P₂S₅ glasses and glass-ceramics in this chapter. All of the samples were prepared by mechanical milling and subsequent heating. The crystal structures and lithium ion conductivities were discussed from the point of view of incorporated elements.

Chapter 5
This chapter describes conclusions of this paper.
Table 1-1 Conductivity of typical inorganic solid electrolyte.

<table>
<thead>
<tr>
<th>Category</th>
<th>Composition</th>
<th>Conductivity at room temperature / S cm$^{-1}$</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxide crystal</td>
<td>La$<em>{0.51}$Li$</em>{0.34}$TiO$_{2.94}$</td>
<td>1.0 $\times$ 10$^{-3}$</td>
<td>14</td>
</tr>
<tr>
<td></td>
<td>Li$_7$La$_3$Zr$<em>2$O$</em>{12}$</td>
<td>3.0 $\times$ 10$^{-4}$</td>
<td>15</td>
</tr>
<tr>
<td></td>
<td>Li$<em>{1.3}$Al$</em>{0.5}$Ti$_{1.7}$(PO$_4$)$_3$</td>
<td>7.0 $\times$ 10$^{-4}$</td>
<td>16</td>
</tr>
<tr>
<td>Oxide glass</td>
<td>24Li$_2$O$\cdot$41B$_2$O$_3$35LiCl</td>
<td>10$^{-6}$</td>
<td>18</td>
</tr>
<tr>
<td>Oxide glass–ceramic</td>
<td>Li$<em>{1.07}$Al$</em>{0.69}$Ti$_{1.46}$(PO$_4$)$_3$</td>
<td>1.3 $\times$ 10$^{-3}$</td>
<td>22</td>
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<tr>
<td></td>
<td>Li$<em>{1.5}$Al$</em>{0.5}$Ge$_{1.5}$(PO$_4$)$_3$</td>
<td>4.0 $\times$ 10$^{-4}$</td>
<td>23</td>
</tr>
<tr>
<td>Sulfide crystal</td>
<td>Li$<em>{3.25}$Ge$</em>{0.25}$P$_{0.75}$S$_4$</td>
<td>2.2 $\times$ 10$^{-3}$</td>
<td>13</td>
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<td></td>
<td>Li$_{10}$GeP$<em>2$S$</em>{12}$</td>
<td>1.2 $\times$ 10$^{-2}$</td>
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<td>Li$_6$P$_5$S$_4$</td>
<td>1.3 $\times$ 10$^{-3}$</td>
<td>32</td>
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<td>Sulfide glass</td>
<td>80Li$_2$S$\cdot$20P$_2$S$_5$</td>
<td>2.1 $\times$ 10$^{-4}$</td>
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<td>60Li$_2$S$\cdot$40SiS$_2$</td>
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<td>37Li$_2$S$\cdot$18P$_5$S$_5$45LiI</td>
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<td>34, 35</td>
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<td>30Li$_2$S$\cdot$26B$_2$S$_3$44LiI</td>
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<td>35Li$_2$S$\cdot$35SiS$_2$30LiBr</td>
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<td>42Li$_2$S$\cdot$28SiS$_2$30LiI</td>
<td>1.8 $\times$ 10$^{-3}$</td>
<td>43</td>
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<td>95(0.6Li$_2$S$\cdot$0.4SiS$_2$)$\cdot$5Li$_6$SiO$_4$</td>
<td>1.7 $\times$ 10$^{-3}$</td>
<td>45</td>
</tr>
<tr>
<td>Sulfide glass–ceramic</td>
<td>80Li$_2$S$\cdot$20P$_2$S$_5$</td>
<td>1.3 $\times$ 10$^{-3}$</td>
<td>49</td>
</tr>
<tr>
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<td>70Li$_2$S$\cdot$30P$_2$S$_5$</td>
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<td>70Li$_2$S$\cdot$28P$_2$S$_5$2GeS$_2$</td>
<td>5.4 $\times$ 10$^{-3}$</td>
<td>53</td>
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References

(1979) 921.


2. Synthesis and characterization of Li$_2$S–P$_2$S$_5$ glass-ceramic electrolytes with LiI

2-1. Introduction

Lithium ion batteries have high energy densities. They have been adopted as power supplies for many types of portable electronic equipment and are also used as storage devices for electrical energy in power systems. But there is a risk of burning under abuse, because they use flammable liquid electrolytes. There is a requirement to improve the safety of batteries; making batteries entirely solid state, using non-flammable solid electrolytes would improve the safety of lithium batteries. It is necessary to develop solid electrolytes with high lithium ion conductivity for realizing all-solid-state lithium batteries.

Many experiments have been conducted to enhance the lithium ion conductivity of sulfide-based solid electrolytes [1–22]. Some sulfide-based crystalline electrolytes have high conductivities at room temperature. The crystals in the Li$_2$S–GeS$_2$–P$_2$S$_5$ system called thio-LISICON have high lithium ion conductivities [7]. The thio-LISICON Li$_{4+y}$Ge$_{1-y}$P$_y$S$_4$ synthesized by solid state reaction has three crystalline phases called region I, region II and region III. Region I is obtained at $0 < y \leq 0.6$ and indexed by a monoclinic superlattice cell of $a \times 3b \times 2c$. The region II phase ($0.6 < y < 0.8$) is indexed by a monoclinic superlattice cell of $a \times 3b \times 3c$ and the region III phase ($0.8 \leq y < 1.0$) is indexed by a monoclinic superlattice cell of $a \times 3b \times 2c$. The region II and the region III have high conductivities of $2.2 \times 10^{-3}$ S cm$^{-1}$ and $10^{-4}$ S cm$^{-1}$ respectively at room temperature [7].

The glass–ceramic electrolytes in the Li$_2$S–P$_2$S$_5$ system also have high lithium ion conductivities [8–13]. The 70Li$_2$S–30P$_2$S$_5$ (mol%) glass-ceramic containing the
Li:P$_2$S$_3$ crystal has a high conductivity of $4.2 \times 10^{-3}$ S cm$^{-1}$ [15, 21]. It was reported that the addition of the third component to the 70Li$_2$S·30P$_2$S$_5$ glass-ceramic affected the conductivities and the crystalline phases [14, 15, 17]. The conductivity of the 70Li$_2$S·30P$_2$S$_5$ glass-ceramic increased to $5.4 \times 10^{-3}$ S cm$^{-1}$ by partial substituting P$_2$S$_3$ for P$_2$S$_5$ [17]. The 75Li$_2$S·25P$_2$S$_5$ glass-ceramic has a thio-LISICON III analog phase and shows the conductivity of $10^{-4}$ S cm$^{-1}$ [11]. The 80Li$_2$S·20P$_2$S$_5$ glass-ceramic has a thio-LISICON II analog phase and shows the conductivity of $1.3 \times 10^{-3}$ S cm$^{-1}$ [11]. It was shown that the conductivity of the thio-LISICON II analog phase was higher than that of the thio-LISICON III analog phase in the Li$_2$S–P$_2$S$_5$ system. A small difference in the heat treatment temperature, however, led to the precipitation of the thio-LISICON III analog phase instead of the thio-LISICON II analog phase in the 80LiS$_2$·20P$_2$S$_5$ glass-ceramic; a heat treatment at slightly higher temperature resulted in the formation of the thio-LISICON III phase [20]. Glass matrices which facilitate precipitation of the thio-LISICON II analog phase would enhance the conductivity of the 80Li$_2$S·20P$_2$S$_5$ glass-ceramic.

For Li$_2$S–P$_2$S$_5$ glasses, the addition of LiI was studied to increase conductivity for glass electrolytes [1, 22]. The lithium ion conductivity of 67Li$_2$S·33P$_2$S$_5$ glass increased from $10^{-4}$ S cm$^{-1}$ to $10^{-3}$ S cm$^{-1}$ by adding 45 mol% LiI [22]. One drawback of the glasses with LiI is their low electrochemical stability; the 67Li$_2$S·33P$_2$S$_5$ glass with LiI was reported to have a electrochemical window of about 2.6 V [22].

In this chapter, preparation of the glasses and glass-ceramics containing LiI was conducted in the compositions of (100−x)(0.7Li$_2$S·0.3P$_2$S$_5$)·xLiI and (100−x)(0.8Li$_2$S·0.2P$_2$S$_5$)·xLiI (mol%) to obtain high lithium ion conductivities. The composition of 70Li$_2$S·30P$_2$S$_5$ and 80Li$_2$S·20P$_2$S$_5$ were selected because of their high lithium ion conductivity. While the Li$_2$S–P$_2$S$_5$ glasses with LiI were prepared by melt quenching in previous reports [1, 22], 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$_7$P$_3$S$_{11}$ based solid solutions is expected to enhance the conductivity of the 70Li$_2$S·30P$_2$S$_5$ glass-ceramics. By the addition of LiI to the 80Li$_2$S·20P$_2$S$_5$ glass-ceramic, it is expected to stabilize the highly conductive crystalline phases precipitated in the glass-ceramic. Precipitation of the thio-LISICON II analog phase in a wide range of the composition is useful for obtaining solid electrolytes with high lithium ion conductivity. The effects of the LiI addition on conductivity and precipitated crystal in the Li$_2$S–P$_2$S$_5$ glass-ceramics were examined.
2-2. Experimental

2-2-1. Sample preparation

The glass-ceramics of \((100-x)(0.7\text{Li}_2\text{S} \cdot 0.3\text{P}_2\text{S}_3) \cdot x\text{LiI}\) \((x = 0, 1, 3, 5, 9, \text{ and } 20)\) and \((100-x)(0.8\text{Li}_2\text{S} \cdot 0.2\text{P}_2\text{S}_5) \cdot x\text{LiI}\) \((x = 0, 2, 5, 10, 15, 20 \text{ and } 30)\) were prepared by mechanical milling and subsequent heat treatment. Reagent-grade \(\text{Li}_2\text{S}\) (Idemitsu Kosan, 99%), \(\text{P}_2\text{S}_5\) (Aldrich, 99%) and \(\text{LiI}\) (Aldrich 99.99%) crystalline powders were used as the starting materials. They were mixed in an agate mortar for 10 min and put into a zirconia pot of 45 ml in volume with 500 zirconia balls of 4 mm in diameter. The pot was mounted on a planetary ball mill apparatus (Fritsch, Pulverisette 7) and mechanical milling was conducted at 500 rpm for 10 hr. The milled samples were heated above their crystallization temperatures. All the processes were carried out in a dry Ar atmosphere.

2-2-2. Characterization

Differential thermal analyses (DTA) were performed using a thermal analyzer (Rigaku, Thermo-plus 8120) to observe crystallization temperatures. The milled samples were sealed in Al pans in a dry Ar atmosphere and heated at 10°C min\(^{-1}\) under \(\text{N}_2\) gas flow. X-ray diffraction (XRD) measurements (\(\text{CuK}_\alpha\)) were carried out using a diffractometer (Rigaku, SmartLab or Rigaku, Ultima V) to identify crystal phases of the milled samples and the heated samples. Raman spectra of the \((100-x)(0.7\text{Li}_2\text{S} \cdot 0.3\text{P}_2\text{S}_3) \cdot x\text{LiI}\) samples were measured using a Raman spectrometer (Jasco, RMP-210) with 532 nm YAG laser. Ionic conductivities were measured for the pelletized samples pressed under 360 MPa. The diameter and the thickness of the pellets were, respectively, 10 mm and about 1.5 mm. Carbon paste was painted as electrodes on both faces of the pellets and stainless steel disks were attached to the pellets as current collectors. The two-electrodes cell was packed in a silica glass tube.
and AC impedance measurements were performed under dry Ar gas flow using an impedance analyzer (Solartron, 1260). The frequency range and the applied voltage were, respectively, 10 Hz to 8 MHz and 50 mV. Cyclic voltammetry was performed for the samples at room temperature using a potentiostat (Solartron 1287). A stainless steel disk as a working electrode and a lithium metal foil as counter and reference electrodes were attached on each face of the pelletized sample. The potential sweep was carried out between −0.1 V and +10 V with a scanning rate of 5 mV s⁻¹.
2-3. Results and discussion

2-3-1. 70Li$_2$S-30P$_2$S$_5$ glass-ceramic with LiI

Mechanical milled samples of (100-x)(0.7Li$_2$S·0.3P$_2$S$_5$)·xLiI were prepared at x = 0, 1, 3, 5, 9 and 10. Fig. 2-1 shows the XRD patterns of the sample powders. Halo patterns were observed for all the samples. It was suggested that amorphous samples were obtained by mechanical milling.

The DTA curves of the milled samples are depicted in Fig. 2-2. Glass transition phenomena occurred between 175 °C and 210 °C, suggesting that the obtained amorphous samples were glasses. The glass transition temperatures (T$_g$) shifted to a 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. 2-3, and thus these exothermic peaks were caused by the crystallization of the glasses. The crystallization temperatures (T$_c$) also shifted to a lower temperature side with increasing the LiI content. It indicates that the addition of LiI to 70Li$_2$S-30P$_2$S$_5$ glasses make it easy to form glass-ceramics at lower temperatures.

The glass-ceramics of (100-x)(0.7Li$_2$S·0.3P$_2$S$_5$)·xLiI (x = 0, 1, 3, 5, 9, and 20) were obtained by heating of the glasses. Fig. 2-3 shows the XRD patterns of the samples heated above T$_c$. The Li$_7$P$_3$S$_{11}$ crystal with high lithium ion conductivity was observed in the 70Li$_2$S·30P$_2$S$_5$ glass-ceramic [11]. The Li$_7$P$_3$S$_{11}$ crystals were also observed in the (100-x)(0.7Li$_2$S·0.3P$_2$S$_5$)·xLiI (x = 1, 3, 5, 9, 20) glass-ceramics. Each diffraction peak of these Li$_7$P$_3$S$_{11}$ crystals was investigated in detail. For example, the most intense peak of the Li$_7$P$_3$S$_{11}$ crystal in all the glass-ceramics was observed at 29.6 degree. There was no obvious shift of the peaks in the composition range 0 ≤ x ≤ 20, which suggests that the added LiI would not form solid solution with the Li$_7$P$_3$S$_{11}$ crystal in the (100-x)(0.7Li$_2$S·0.3P$_2$S$_5$)·xLiI glass-ceramics. While the intensity of the XRD peaks
attributable to the Li$_7$P$_3$S$_{11}$ crystal was decreased with increasing the LiI content, the intensity of unknown peaks increased. These unknown peaks did not correspond to the XRD patterns of the series of the thio-LISICON Li$_{4-x}$Ge$_x$P$_x$S$_4$ and Li$_{3+5x}$P$_1-x$S$_4$ or to the patterns of α, β and γ-phases of Li$_3$PS$_4$ [7, 9, 19]. Weak peaks attributable to LiI crystals were observed in the glass–ceramics added with LiI.

The Raman spectra of the glasses and glass–ceramics are presented in Fig. 2-4. The samples of glasses had a peak at 410 cm$^{-1}$ and a weak shoulder at 425 cm$^{-1}$. The peaks at 410 cm$^{-1}$ and 425 cm$^{-1}$ are attributable to the P$_2$S$_7^{4-}$ and PS$_4^{3-}$ ions, respectively [3]. The glass–ceramics at $x = 0$ and 5 showed similar spectra to that of the glasses. The glass–ceramic at $x = 20$ had the obvious peak at 425 cm$^{-1}$, indicating that the amount of PS$_4^{3-}$ ions were increased. It suggests that the unknown phase observed in the XRD measurements would be a crystal mainly composed of PS$_4^{3-}$ ions. The total lithium ion concentration in the glasses was increased from 33 to 35 mol% by the addition of 20 mol% LiI to the sulfide glass. It is supposed that the excess amounts of lithium ion incorporated by the added LiI have a tendency of precipitation of the PS$_4^{3-}$-containing phases by crystallization.

The conductivities at room temperature for the (100–$x$)(0.7Li$_2$S·0.3P$_2$S$_5$)·$x$LiI glasses and glass–ceramics are portrayed in Fig. 2-5. The conductivity of the 70Li$_2$S·30P$_2$S$_5$ glass was 1.3 × 10$^{-4}$ S cm$^{-1}$. It was slightly higher than the conductivities of the 70Li$_2$S·30P$_2$S$_5$ glass reported in previous studies [11, 13]. The conductivities of glasses increased monotonically with increasing the LiI content. The glass at $x = 20$ showed the highest conductivity of 5.6 × 10$^{-4}$ S cm$^{-1}$. The similar enhancement of the conductivity of the Li$_2$S–P$_2$S$_5$ glasses by the addition of LiI was reported at the composition of 67Li$_2$S·33P$_2$S$_5$ [22]. However, the conductivity of the glass of $x = 20$ in this study was about half of that of the melt quenched 67Li$_2$S·33P$_2$S$_5$ glass with 45 mol% LiI. It would be caused by the differences of the Li concentrations and the
measurement methods. The total Li concentrations of the 70Li$_2$S·30P$_2$S$_5$ glass with 20 mol% LiI and the 67Li$_2$S·33P$_2$S$_5$ glass with 45 mol% LiI were 35 mol% and 36 mol% respectively. The conductivity of the 70Li$_2$S·30P$_2$S$_5$ glass with 20 mol% LiI was measured for a powder compressed pellet, and thus the conductivity included a grain-boundary impedance component. The lower Li concentration and the additional grain-boundary contribution would cause the lower conductivity of the 70Li$_2$S·30P$_2$S$_5$ glass with 20 mol% LiI. The conductivity of 70Li$_2$S·30P$_2$S$_5$ glass–ceramic was $4.2 \times 10^{-3}$ S cm$^{-1}$, which was the same value as the previous reports [15, 17]. The Li$_2$P$_3$S$_{11}$ crystals still remained in the glass–ceramics with LiI as shown in XRD measurements (Fig. 2-3), while the conductivity of the glass–ceramics was dramatically decreased with increasing the LiI content. The formation of the unknown crystal probably caused the decrease of conductivity of the glass–ceramics. The conductivity of the glass-ceramic of x = 20 was slightly higher than that of x = 9 in spite of the increasing the intensity of the XRD peaks attributable to the unknown crystal as shown in Fig. 2-3. One possible reason is the existence of the glass components remaining in the glass–ceramic. The high conductivity of the glass of x = 20 might increase the conductivity of the glass–ceramic of x = 20.

Fig. 2-6 shows cyclic voltammograms of the glass at the composition x = 20. Fig. 2-6 (a) shows the first cycle and Fig. 2-6 (b) shows the second cycle. The potential was swept between open circuit voltage and +10 V vs. Li$^+/Li$. A very small anodic current of below 1 $\mu$A was observed in the first cycle. The small anodic current was also observed in the Li$_2$S–P$_2$S$_5$ glasses and glass–ceramics [10, 12]. One of the possible origins of the current is oxidation of ions such as S$^{2-}$ and I$^-$. On the subsequent cathodic sweep, cathodic current was not observed. In the second cycle, the anodic current almost disappeared. It is suggested that the species oxidized during the first anodic sweep was stable and almost no oxidation occurred in the subsequent cycle.
Fig. 2-7 shows also cyclic voltammogram after the sweeps shown in Fig. 2-6. The potential was swept between −0.1 V and +10 V vs. Li+/Li. A large cathodic current was observed in a cathodic sweep to −0.1 V and a large anodic peak was observed in an anodic sweep up to +0.1 V. The cathodic current and the anodic current suggest that lithium deposition and dissolution occurred. In this study, the potential was swept up to +10 V and no obvious current was observed between +5 V and +10 V. It is indicated that the 80(0.7Li$_2$S·0.3P$_2$S$_5$)·20LiI glass had a wide electrochemical window up to 10 V vs. Li+/Li.
Fig. 2-1 XRD patterns of the $(100-x)(0.7Li_2S\cdot0.3P_2S_5)\cdot xLiI$ samples prepared by mechanical milling.
Fig. 2-2 DTA curves of the (100−x)(0.7Li₂S-0.3P₂S₅)-ₓLiI samples prepared by mechanical milling.
Fig. 2-3 XRD patterns of the (100-x)(0.7Li2S·0.3P2S5)-xLiI samples prepared by heat treatment.
Fig. 2-4 Raman spectra of the \((100-x)(0.7\text{Li}_2\text{S}-0.3\text{P}_2\text{S}_5)\cdot x\text{LiI}\) glasses and glass-ceramics.
Fig. 2-5 Composition dependence conductivities at room temperature for the $(100-x)(0.7\text{Li}_2\text{S} \cdot 0.3\text{P}_2\text{S}_5)\cdot x\text{LiI}$ glasses and glass-ceramics.
Fig. 2-6 Cyclic voltammograms of the 80(0.7Li₂S·0.3P₂S₅)·20LiI glass of (a) the first cycle and (b) the second cycle. The scan rate was 5 mV s⁻¹. The potential was swept from open circuit voltage to +10 V.
Fig. 2-7 Cyclic voltammogram of the 80(0.7Li₂S·0.3P₂S₅)·20LiI glass. The scan rate was 5 mV s⁻¹. The potential was swept between from −0.1 V and +10 V.
2-3-2. 80Li₂S·20P₂S₅ glass-ceramic with LiI

Powder samples of (100−x)(0.8Li₂S·0.2P₂S₅)·xLiI (x = 0, 2, 5, 10, 15, 20 and 30) were prepared by mechanical milling. The XRD patterns of the mechanical milled samples are presented in Fig. 2-8. The diffraction peaks attributable to the Li₂S crystal and halo patterns were observed for all samples. It was suggested that amorphous powders containing a certain amount of the Li₂S crystal were obtained. The intensity of the peaks of Li₂S decreased with increasing x, the LiI content. It would be caused by the decrease of the Li₂S content in the starting materials. A weak peak attributable to the LiI crystal remained at x = 30.

The DTA curves of the milled samples are shown in Fig. 2-9. Glass transition phenomena were observed between 140 °C and 220 °C, indicating that these amorphous samples were glasses. Two exothermic peaks were observed between 200 °C and 300 °C at x = 0, 2, 5, 10 and 15. The peaks of the higher temperature disappeared at x = 20 and 30. The glass samples were heated just above crystallization temperatures corresponding to the lower exothermic peaks.

Fig. 2-10 shows the XRD patterns of the samples prepared using heat treatment. Some crystalline peaks were observed, suggesting that glass-ceramics were obtained. As shown in Fig. 2-9, the crystallization temperatures shifted to a lower temperature side with increasing the LiI content. It indicates that the addition of LiI to the 80Li₂S·20P₂S₅ glass makes it easy to form glass-ceramics at lower temperatures. In the 80Li₂S·20P₂S₅ glass-ceramic (x = 0), the thio-LISICON III analog phase was mainly precipitated. The peaks attributable to Li₂S crystal and thio-LISICON II analog phase were also observed, but a peak at 19° was not identified. At x = 2, 5, 10 and 15, the peaks of the thio-LISICON II analog phase was dominant. The addition of LiI to the 80Li₂S·20P₂S₅ glass-ceramic was effective in precipitating the thio-LISICON II analog phase. The full width at half maximum (FWHM) of the XRD peaks attributable to the
thio-LISICON II analog phase increased with increasing the LiI content. For instance, FWHMs of the peak at 20° for the glass–ceramics at $x = 2$ and 15 were respectively 0.37° and 0.50°. At $x = 20$, the intensity of the peaks of the thio-LISICON II analog phase decreased, and the unknown peaks observed in the $(100-x)(0.7Li_2S\cdot0.3P_2S_5)\cdot x$LiI glass–ceramics appeared. At $x = 30$, the peaks of the thio-LISICON II analog phase almost disappeared, and the peaks attributable to the Li$_6$PS$_5$I crystal were observed. The peaks due to the LiI crystal became clearer than that of the glass. It is considered that the LiI crystal remaining in the glass grew by the heat treatment.

Fig. 2-11 shows the magnification of the XRD patterns of $x = 2, 5, 10$ and 15. The peaks of the thio-LISICON II analog phase shifted to a lower degree side with increasing the LiI content. It indicates the expansion of the crystal lattice. Although further structural analyses are needed, one possible reason is the formation of a solid solution by the substitution of $I^-$ ions into the lattice of the thio-LISICON II analog phase. The effective ionic radii of $I^-$ and $S^{2-}$ ions are 220 and 184 pm respectively [23]. It is considered that the substitution of $I^-$ ions for $S^{2-}$ ions expands the crystal lattice.

The composition dependence of electrical conductivities at 25 °C for the glasses and the glass–ceramics are depicted in Fig. 2-12. The conductivity of the glass at $x = 0$ was $2.9 \times 10^{-4} \text{ S cm}^{-1}$, which was almost the same value as the previous report [11]. The conductivities of the glasses increased with increasing the LiI content, the highest conductivity of $6.5 \times 10^{-4} \text{ S cm}^{-1}$ was observed at $x = 20$. It is considered that the increase of the conductivity was caused by the increase of Li$^+$ ion content in the glasses. At $x = 30$, the conductivity of the glass decreased to $1.5 \times 10^{-4} \text{ S cm}^{-1}$. The low conductivity at $x = 30$ would be caused by the LiI crystals remaining in the glass as shown in Fig. 2-8. The conductivity of the glass–ceramic at $x = 0$ was $8.2 \times 10^{-4} \text{ S cm}^{-1}$, and it increased to the values above $2 \times 10^{-3} \text{ S cm}^{-1}$ in the range from $x = 2$ to 15. The glass–ceramic at $x = 5$ showed the highest conductivity of $2.7 \times 10^{-3} \text{ S cm}^{-1}$. The high
conductivities of the glass-ceramics would be mainly due to the precipitations of the thio-LISICON II analog phase. At $x = 20$ and $30$, the conductivities of the glass-ceramics decreased steeply.

The conductivities of the glass-ceramics in the range from $x = 2$ to $15$ showed almost the same values despite great change of the LiI contents. It is considered that the conductivities of the glass-ceramics were affected by the Li$^+$ ion content, the crystallinity of the thio-LISICON II analog phase and the substitution of I$^-$ ions. Firstly, the increase of Li$^+$ ion content in the glass-ceramic would enhance the conductivity, because Li$^+$ ions are the carrier of current. The total lithium concentrations in the glass-ceramics at $x = 2$ and $15$ were calculated to be $42.2$ mol$\%$ and $42.8$ mol$\%$ respectively. So, the increase of LiI content would increase the conductivity from the viewpoint of the concentration of Li$^+$ ions. Secondly, the improvement of the crystallinity of the thio-LISICON II analog phase would enhance the conductivity, because the glass-ceramics with the thio-LISICON II analog phase showed high conductivities. FWHM of the XRD peaks attributable to the thio-LISICON II analog phase increased with increasing the LiI content, suggesting that a large LiI content degraded the crystallinity of the thio-LISICON II analog phase. Thus, the increase of LiI content would decrease the conductivity from the viewpoint of the crystallinity of the thio-LISICON II analog phase. Thirdly, the substitution of I$^-$ ions into the lattice of the thio-LISICON II analog phase would enhance the conductivity. As mentioned above, it is considered that the substitution of I$^-$ ions for S$^{2-}$ ions expands the lattice of the crystal, and thus the size of bottle neck for Li$^+$ ion pass would be increased. Furthermore, the substitution would induce lattice defects available for transfer of Li$^+$ ions. Therefore, the increase of LiI content would increase the conductivity from the viewpoint of the substitution. The conductivities of the glass-ceramics in the range from $x = 2$ to $15$ would be affected by those three factors, and showed almost the same values.
The influence of heat treatment temperatures on crystal phases and conductivities of the glass-ceramics was investigated. Fig. 2-13 shows the XRD patterns of the 90(0.8Li$_2$S·0.2P$_2$S$_5$)·10LiI glass-ceramics obtained by heat treatment at different temperatures of 206, 224 and 292 °C above the crystallization temperature. The conductivities of the samples at 25 °C are shown in Fig. 2-14 with the DTA curve of the 90(0.8Li$_2$S·0.2P$_2$S$_5$)·10LiI glass. The diffraction peaks of the thio-LISICON II analog phase and the Li$_2$S crystal were observed in all samples in Fig. 2-13. The peaks attributable to the Li$_6$PS$_5$I crystal were observed in the samples obtained by heat treatment at 224 °C and 292 °C. The intensity of Li$_6$PS$_5$I peaks increased with increasing the temperature of heat treatment. The conductivity decreased with increasing the temperature of heat treatment in Fig. 2-14. The precipitation of the Li$_6$PS$_5$I crystal with low conductivity [24] would cause a decrease of conductivity. However, the thio-LISICON II analog phase was precipitated in a wide temperature range. It was suggested that the addition of LiI to the 80Li$_2$S·20P$_2$S$_5$ glass-ceramic made it possible to precipitate the thio-LISICON II analog phase stably over crystallization temperature.

The cyclic voltammogram of the glass-ceramic electrolyte at x = 5 is shown in Fig. 2-15. The cathodic and anodic currents correspond to lithium deposition and dissolution were observed in the potential range from $-0.1$ V to $+0.1$ V. There was not obvious cathodic nor anodic peak between $+0.1$ V and $+10$ V, suggesting that the glass-ceramic had a wide electrochemical window.
Fig. 2-8 XRD patterns of the \((100-x)(0.8\text{Li}_2\text{S}-0.2\text{P}_2\text{S}_5)\cdot x\text{LiI}\) samples prepared by mechanical milling.
Fig. 2-9 DTA curves of the \((100-x)(0.8\text{Li}_2\text{S}-0.2\text{P}_2\text{S}_5)-x\text{LiI}\) samples prepared by mechanical milling.
Fig. 2-10 XRD patterns of the \((100-x)(0.8Li_2S\cdot0.2P_2S_5\cdot xLiI)\) glass-ceramics prepared by heat treatment.
Fig. 2-11 Magnification of XRD patterns of the (100−x)(0.8Li2S·0.2P2S5)·xLiI glass–ceramics prepared by heat treatment.
Fig. 2-12 Composition dependence of conductivities at 25 °C for the \((100-x)(0.8\text{Li}_2\text{S} \cdot 0.2\text{P}_2\text{S}_5)\cdot x\text{LiI}\) glasses and glass-ceramics.
Fig. 2-13 XRD patterns of the 90(0.8Li₂S·0.2P₂S₅)·10LiI glass-ceramics prepared by heat treatment at different temperatures.
Fig. 2-14 Conductivities at 25 °C of the 90(0.8Li₂S·0.2P₂S₅)·10LiI glass-ceramics prepared by heat treatment at different temperatures. DTA curve of the 90(0.8Li₂S·0.2P₂S₅)·10LiI glass is shown for reference.
Fig. 2-15 Cyclic voltammogram of the 95(0.8Li$_2$S·0.2P$_2$S$_5$)·5LiI glass-ceramic. The scan rate was 5 mV s$^{-1}$. The potential was swept between −0.1 and +10 V.
2-4. Summary

LiI was incorporated into the glass and glass-ceramic electrolytes of Li$_2$S–P$_2$S$_5$ system with the aim of enhancing the electrical conductivity.

Glasses and glass-ceramics of (100–x)(0.7Li$_2$S·0.3P$_2$S$_5$)·xLiI were prepared by mechanical milling and subsequent heat treatment in the composition range from x = 0 to 20. No crystal phase of LiI remained in the glasses. All the glasses and glass-ceramics exhibited the P$_2$S$_7^{4−}$ ions. The Li$_7$P$_{311}$ crystals were precipitated in all the glass-ceramics, but LiI did not form solid solutions with the crystals. An unknown crystal containing PS$_{43}^{3−}$ ions were mainly precipitated in the glass-ceramics with increasing the LiI content. The conductivity of glasses increased with increasing the LiI content and it was improved to $5.6 \times 10^{-4}$ S cm$^{-1}$ at the glass at x = 20. The conductivity of glass-ceramics sharply decreased from $4.2 \times 10^{-3}$ S cm$^{-1}$ with increasing the LiI content. The 80(0.7Li$_2$S·0.3P$_2$S$_5$)·20LiI glass had wide electrochemical window up to 10 V vs. Li$^+$/Li.

The glass-ceramic electrolytes of (100–x)(0.8Li$_2$S·0.2P$_2$S$_5$)·xLiI (x = 0, 2, 5, 10, 15, 20 and 30) were prepared by mechanical milling and subsequent heat treatment. The crystallization temperatures of the glass-ceramics decreased with increasing the LiI content. It indicates that the added LiI makes it easy to form glass-ceramics at lower temperatures. Li$_2$S crystals which remained in the precursor glasses were observed in all the glass-ceramics. The thio-LISICON III analog phase with the conductivity of $10^{-4}$ S cm$^{-1}$ was mainly precipitated at x = 0, whereas the thio-LISICON II analog phase with the conductivity of $10^{-3}$ S cm$^{-1}$ was precipitated in the range from x = 2 to 15. The thio-LISICON II analog phase was obtained in a wide temperature range of heat treatment. It was suggested that the addition of LiI to the 80Li$_2$S·20P$_2$S$_5$ glass-ceramic was effective in precipitating the thio-LISICON II analog phase stably over the crystallization temperature. The XRD peaks of the thio-LISICON II analog
phase shifted to smaller angles with increasing the LiI content, suggesting that a solid solution was formed. At $x = 20$, the thio-LISICON II analog phase was decreased, and the unknown phase appeared. At $x = 30$, the thio-LISICON II analog phase almost disappeared, and the Li$_8$PS$_4$ crystal was observed. High conductivities above $2 \times 10^{-3}$ S cm$^{-1}$ were observed in a wide composition range from $x = 2$ to 15. It is revealed that the addition of LiI to the 80Li$_2$S·20P$_2$S$_5$ glass-ceramic brought about an increase of conductivity. The glass-ceramic electrolyte at $x = 5$ with the highest conductivity of $2.7 \times 10^{-3}$ S cm$^{-1}$ showed a wide electrochemical window of about 10 V.

In the (100−$x$)(0.7Li$_2$S·0.3P$_2$S$_5$)·$x$LiI glass-ceramics, the added LiI did not form solid solution with the Li$_3$P$_7$S$_{11}$ crystal. On the other hand, it was suggested that the added LiI formed solid solution with the thio-LISICON II analog phase in the (100−$x$)(0.8Li$_2$S·0.2P$_2$S$_5$)·$x$LiI glass-ceramics. The difference of crystal phases precipitated in the glass-ceramics would affect the formation of solid solution. The thio-LISICON II analog phase is precipitated also in the 87.5Li$_2$S·12.5P$_2$S$_5$ [11]. It is suggested that the thio-LISICON II analog phase is precipitated in the composition range of a high Li content in the binary system Li$_2$S–P$_2$S$_5$. The addition of LiI to the 80Li$_2$S·20P$_2$S$_5$ glass-ceramic increases the Li content. Therefore, added LiI would not disturb the precipitation of the thio-LISICON II analog phase, and substitution of I$^-$ ions into the lattice of the thio-LISICON II analog phase would be promoted with increasing the LiI content.

Incorporation of LiI into the 70Li$_2$S·30P$_2$S$_5$ glass-ceramic decreased the conductivity, while incorporation of LiI into the 80Li$_2$S·20P$_2$S$_5$ glass-ceramic was effective in increasing conductivity. The crystal phases precipitated in the glass-ceramics affected the conductivity.
2-5. References


3. Synthesis and characterization of Li$_2$S–P$_2$S$_5$ glass–ceramic electrolytes with LiBr

3-1. Introduction

Electric power generation using renewable energy such as sunlight and wind is increasing. Electrical storage will be an important function of the power system because power is not supplied continuously by such renewable energy resources. Batteries are suitable for power storage because of their high energy efficiencies. Lithium ion batteries with high energy densities are expected to be used in large-scale power storage systems. Safety and reliability are strongly required for large storage systems, while lithium ion batteries present the risk of burning because of their flammable liquid electrolytes. All-solid-state batteries using non-flammable solid electrolytes are expected to improve the safety and reliability of lithium ion batteries. However, the conductivities of the solid electrolytes are not sufficiently high. Solid electrolytes with high lithium ion conductivities and wide electrochemical windows are necessary to put all-solid-state batteries to practical use.

Sulfide-based electrolytes as lithium ion conductors have been investigated [1–12]. The crystals in the Li$_2$S–GeS$_2$–P$_2$S$_5$ system called thio-LISICON have conductivities of $10^{-4}$ – $10^{-3}$ S cm$^{-1}$ at room temperature [5]. Recently, Kanno et al. reported a new crystal of Li$_{10}$GeP$_2$S$_{12}$ showing extremely high conductivity of $1.2 \times 10^{-2}$ S cm$^{-1}$ [13]. The glass electrolytes in the Li$_2$S–P$_2$S$_5$ system have conductivities of $10^{-4}$ S cm$^{-1}$ at room temperature. They are enhanced by the addition of a lithium halide [1]. The lithium ion conductivity of 70Li$_2$S–30P$_2$S$_5$ glass increased from $1.3 \times 10^{-4}$ S cm$^{-1}$ to $5.6 \times 10^{-4}$ S cm$^{-1}$ by the addition of 20 mol% LiI as mentioned in
Chapter 2. Presumably, the enhancement of conductivity resulted from the increase of the total lithium ion concentration in the glass. The glass-ceramic electrolytes in the Li$_2$S–P$_2$S$_5$ system also show high lithium ion conductivities [6–9]. Above all, 70Li$_2$S·30P$_2$S$_5$ glass-ceramic containing the Li$_7$P$_3$S$_{11}$ crystal has high conductivity of 4.2 × 10$^{-3}$ S cm$^{-1}$ [6]. We added LiI to the 70Li$_2$S·30P$_2$S$_5$ glass-ceramic in expectation of increased conductivity, but the conductivity decreased sharply with increasing LiI contents, as described in Chapter 2. Unknown crystal phase was precipitated in the glass-ceramic added with LiI, although the fraction of the Li$_7$P$_3$S$_{11}$ crystal with a high conductivity decreased. A solid solution of LiI in the Li$_7$P$_3$S$_{11}$ crystal was not confirmed. The conductivity of the 70Li$_2$S·30P$_2$S$_5$ glass-ceramic would be enhanced if the lithium ion concentration could be increased without decreasing the Li$_7$P$_3$S$_{11}$ crystal phase.

In this study, LiBr was added to the 70Li$_2$S·30P$_2$S$_5$ glass-ceramic. The effective ionic radii of I$^-$, Br$^-$ and S$^{2-}$ are, respectively, 220, 196 and 184 pm [14]. LiBr might be dissolved in the Li$_7$P$_3$S$_{11}$ crystal because the radius of Br$^-$ is smaller than that of I$^-$. Moreover, it is close to that of S$^{2-}$. The solid solution is expected to reduce the precipitation of other crystal phases that would decrease the glass-ceramic conductivity. The addition of LiBr increases the Li content in the 70Li$_2$S·30P$_2$S$_5$ glass-ceramic. It is therefore expected that the addition of LiBr to the 70Li$_2$S·30P$_2$S$_5$ glass-ceramic enhances the conductivity. We synthesized the glass-ceramic electrolytes by mechanical milling and subsequent heat treatment. The crystalline phases and the conductivities of the glass-ceramics were examined. An all-solid-state cell was fabricated. Then its charge-discharge performance was investigated.
3-2. Experimental

3-2-1. Sample preparation

(100−x)(0.7Li₂S·0.3P₂S₅)•xLiBr (mol%) (x = 0, 5, 10, 12.5, 15 and 20) glasses were synthesized by mechanical milling. Reagent-grade Li₂S (99.9 %; Nippon Chemical), P₂S₅ (99 %; Aldrich) and LiBr (99.999 %; Aldrich) were used as starting materials. They were mixed in an agate mortar for 10 min and put into a 45 ml ZrO₂ pot with 500 ZrO₂ balls of 4 mm diameter. The pot was mounted on a planetary ball mill apparatus (Pulverisette 7; Fritsch). Then the materials were milled at 500 rpm for 10, 20, or 30 hr. Some samples labeled as “(A+B)+C” were synthesized using two-step milling: A and B were mixed and milled for 10 hr, then the obtained compound and C were mixed and milled for 10 hr. All processes were conducted in a dry Ar atmosphere. Glass-ceramic samples were obtained by heating the milled samples.

3-2-2. Characterization

Differential thermal analyses (DTA) were conducted using a thermal analyzer (Thermo-plus 8120; Rigaku) to observe crystallization temperatures. The glass samples were sealed in Al pans in an Ar-filled glove box and heated at 10 °C min⁻¹ under N₂ gas flow up to 400 °C. X-ray diffraction (XRD) measurements (CuKα) were performed using a diffractometer (SmartLab; Rigaku) to identify crystal phases of the glass samples and the glass-ceramic samples. Ionic conductivities were measured for the pelletized samples pressed under 360 MPa. The pellet diameter and thickness were, respectively, 10 mm and about 1.5 mm. Carbon paste was painted as electrodes on both faces of the pellets and stainless steel disks were attached to the pellets as current collectors. The prepared two-electrode cell was packed in a silica glass tube. Then AC impedances were
measured under dry Ar gas flow using an impedance analyzer (1260; Solartron). The frequency range and the applied voltage were, respectively, 10 Hz to 8 MHz and 50 mV. The electrochemical stability of the glass-ceramic sample was evaluated using cyclic voltammetry at room temperature using a potentiostat (1287; Solartron). A stainless steel disk as a working electrode and a lithium metal foil as a counter and reference electrode were attached to each face of the pelletized sample. The potential was swept between −0.1 V and +10 V with a scanning rate of 5 mV s⁻¹. An all-solid-state two electrode cell was assembled using the glass-ceramic sample as an electrolyte. The positive electrode was prepared by mixing two powders of LiCoO₂ as an active material and the glass-ceramic as an electrolyte. The LiCoO₂ particles were coated with LiNbO₃ thin film in advance because the LiNbO₃-coated LiCoO₂ shows good charge-discharge performance in all-solid-state batteries using a sulfide-based electrolyte [15]. An indium foil was used as a negative electrode.
3-3. Results and discussion

The XRD patterns of the \((100-x)(0.7\text{Li}_2\text{S} \cdot 0.3\text{P}_2\text{S}_5)\cdot x\text{LiBr}\) samples prepared by mechanical milling for 10 hr are presented in Fig. 3-1. Halo patterns were observed for all the samples, indicating that amorphous powders with no crystal phase were obtained in the composition of \(0 \leq x \leq 20\).

Fig. 3-2 shows DTA curves of the milled samples. Glass transition phenomena occurred between 180 and 220 °C, which suggested that the amorphous powders obtained by milling were glasses. Marked exothermic peaks were observed between 230 and 260 °C. These peaks were regarded as resulting from crystallization of the glasses because the samples heated to temperatures just above these temperatures exhibited crystalline XRD patterns as depicted in Fig. 3-3. The glass transition temperatures and the crystallization temperatures were shifted to a lower temperature with increasing LiBr content. The shifts of the temperatures would result from the change of the glass composition and the glass structure. Results suggest that the milled LiBr was not simply amorphous, but mainly entered into the binary \(\text{Li}_2\text{S} - \text{P}_2\text{S}_5\) glass.

The XRD patterns of the \((100-x)(0.7\text{Li}_2\text{S} \cdot 0.3\text{P}_2\text{S}_5)\cdot x\text{LiBr}\) samples prepared using heat treatment are depicted in Fig. 3-3. Several crystalline peaks were observed, indicating that glass–ceramics were obtained. The \(\text{Li}_7\text{P}_3\text{S}_{11}\) crystals with high lithium ion conductivity were precipitated in all samples. The \(\text{Li}_7\text{P}_3\text{S}_{11}\) crystal peaks maintained almost identical intensity in the composition range from \(x = 0\) to 15. At \(x = 20\), the intensity of the peaks of the \(\text{Li}_7\text{P}_3\text{S}_{11}\) crystal was weakened slightly, suggesting that the \(\text{Li}_7\text{P}_3\text{S}_{11}\) crystallinity was degraded. No marked shift of the peaks caused by the \(\text{Li}_7\text{P}_3\text{S}_{11}\) crystal was observed. However, the formation of a solid solution of LiBr in the \(\text{Li}_7\text{P}_3\text{S}_{11}\) crystal cannot be denied. Br⁻ ions would be partially substituted for \(\text{S}^{2-}\) ions to form a \(\text{Li}_{7-x}\text{P}_3\text{S}_{11-x}\text{Br}_x\) crystal if LiBr is dissolved in the
LiP₃S₁₁ crystal. The shift of the diffraction peaks caused by the solid solution must be slight because the ionic radii of Br⁻ and S²⁻ are close [14]. The little shift of the diffraction peaks would not be clearly observed using our laboratory XRD instruments. Further structural analyses are necessary to confirm the solid solution.

The peaks attributable to LiBr crystal were also observed in samples containing LiBr as a starting material. The intensity of the peaks increased concomitantly with increasing LiBr content. The LiBr crystals in the glass-ceramics were not caused by starting crystals, but were precipitated from the glasses because the crystal phase of LiBr disappeared completely during mechanical milling, as shown in Fig. 3-1. The LiBr crystal peak at 28.1 ° for x = 10 and 12.5 showed asymmetric broadening to a larger angle side. The peak resulted from diffraction from (111) planes of LiBr crystals with a face-centered cubic structure. Asymmetric broadening of the peak was regarded as resulting from stacking faults on the (111) planes [16–18]. Consequently, the LiBr crystals precipitated in the glass-ceramic at x = 10 and 12.5 would have stacking faults on the (111) planes. The peak at 26.5° was attributable to carbon paste (graphite) painted on the pellets to facilitate AC impedance measurements.

The composition dependence of electrical conductivities at 25 °C for the glasses and glass-ceramics are portrayed in Fig. 3-4. The glass conductivities increased concomitantly with increasing LiBr content. The conductivity at x = 20 was 3.1 × 10⁻⁴ S cm⁻¹. The increase of the conductivity is expected to result from the increased Li⁺ ion content in the glasses. The glass-ceramic conductivities also increased concomitantly with increasing LiBr content between x = 0 to 10. The conductivity of the glass-ceramic at x = 0 was 3.9 × 10⁻³ S cm⁻¹. It increased to 6.5 × 10⁻³ S cm⁻¹ at x = 10. In the composition range of x = 12.5 to 20, the glass-ceramic conductivities were decreased concomitantly with increasing LiBr contents.
The change in the conductivity of glass–ceramic was inferred to result from the increased Li$^+$ ion content, the precipitation of the Li$_7$P$_3$S$_{11}$ crystal, the increased conductivity of the glass remaining in the glass–ceramic, and the precipitation of LiBr crystal. The increase in the Li$^+$ ion content would increase the conductivity of glass–ceramic because Li$^+$ ions are only charge carriers. The precipitation of Li$_7$P$_3$S$_{11}$ crystal provides high conductivity with the glass–ceramic because the Li$_7$P$_3$S$_{11}$ crystal has extremely high conductivity [6]. Higher conductivity of glass would enhance the conductivity of corresponding glass–ceramic. The LiBr crystal precipitation is generally regarded as decreasing the conductivity of glass–ceramic because of its low conductivity of $9 \times 10^{-9}$ S cm$^{-1}$ at 25 °C. [19]. However, the LiBr crystal might not decrease the conductivities excessively if it has stacking faults in its structure. In the range of $x = 0$ to $10$, the Li$_7$P$_3$S$_{11}$ crystal caused high conductivity of glass–ceramic. The Li$^+$ ions as charge carriers were increased with the non-crystallized LiBr component. The conductivity of precursor glass increased. Therefore, the conductivity of glass–ceramic was enhanced. In addition, the possibility exists that a solid solution of LiBr in the Li$_7$P$_3$S$_{11}$ crystal improved the conductivity. In the range of $x = 12.5$ to $20$, the Li$_7$P$_3$S$_{11}$ crystal provides high conductivity to glass–ceramic in the same manner between $x = 0$ to $10$. However, the increase of the crystallinity of LiBr phase decreased glass–ceramic conductivity despite the increase in the Li$^+$ ion content. In addition, at $x = 20$, the decrease in the conductivity was accelerated by the degradation of the Li$_7$P$_3$S$_{11}$ crystal crystallinity.

As portrayed in Fig. 3-4, the highest conductivity of $6.5 \times 10^{-3}$ S cm$^{-1}$ was obtained for the 90(0.7Li$_2$S·0.3P$_2$S$_3$)·10LiBr glass–ceramic. We sought to enhance the conductivity of the 90(0.7Li$_2$S·0.3P$_2$S$_3$)·10LiBr glass–ceramic by changing the milling process. Fig. 3-5 shows XRD patterns of the 90(0.7Li$_2$S·0.3P$_2$S$_3$)·10LiBr glasses prepared using various milling processes. The samples labeled as “10hMM”,
"20hMM", and "30hMM" were milled, respectively, for 10, 20, and 30 hr. The samples labeled as "(Li$_2$S+P$_2$S$_5$)+LiBr", "(LiBr+P$_2$S$_5$)+Li$_2$S", and "(Li$_2$S+LiBr)+P$_2$S$_5$" were milled using two-step milling defined in "Experimental". Halo patterns were observed for all samples. Glasses were obtained despite the difference in milling processes. An unknown peak was observed for the (Li$_2$S+LiBr)+P$_2$S$_5$ sample, and also for the "(Li$_2$S+LiBr)" sample, suggesting that the peak resulted from a compound of Li$_2$S and LiBr. The peak assignment has not been clarified yet.

The DTA curves of the 90(0.7Li$_2$S·0.3P$_2$S$_5$)·10LiBr glasses prepared using various milling processes are depicted in Fig. 3-6. The exothermic peaks attributable to crystallization were observed between 220 and 230 °C. Glass transition phenomena were observed at about 195 °C in all samples. The glasses prepared by milling for over 20 hr except for the (Li$_2$S+LiBr)+P$_2$S$_5$ glass showed a clearer glass transition than the 10hMM glass. Milling for 20 or 30 hr was believed to be effective for obtaining homogeneous glasses [8].

Fig. 3-7 shows XRD patterns of the 90(0.7Li$_2$S·0.3P$_2$S$_5$)·10LiBr glasses prepared using various milling processes and subsequent heat treatment. Each sample was heated at a temperature between 250 and 270 °C. The peaks attributable to the Li$_7$P$_3$S$_{11}$ crystal and LiBr crystal were observed for all samples. The intensities of the peaks attributable to LiBr crystal in the 10hMM and (Li$_2$S+P$_2$S$_5$)+LiBr samples were slightly larger than those in the other samples. Results suggest that the milling period for the compounds containing LiBr affected the LiBr crystal precipitation in the glass-ceramic. In the (Li$_2$S+LiBr)+P$_2$S$_5$ sample, the peak intensity in the Li$_7$P$_3$S$_{11}$ crystal was weakened. A peak attributable to Li$_2$S crystal was observed.

Table 3-1 shows the conductivities at 25 °C for the 90(0.7Li$_2$S·0.3P$_2$S$_5$)·10LiBr glasses and glass-ceramics prepared using various
milling processes and subsequent heat treatment. The 90(0.7Li$_2$S·0.3P$_2$S$_5$)·10LiBr glass–ceramics milled for over 20 hr showed extremely high conductivity of about 8 × 10$^{-3}$ S cm$^{-1}$, except for the (Li$_2$S+LiBr)+P$_2$S$_5$ glass–ceramic. In the two-step milling samples, glass–ceramics with high conductivities tended to be obtained from glasses with high conductivities. The highest conductivity of 8.4 × 10$^{-3}$ S cm$^{-1}$ was obtained for the (LiBr+P$_2$S$_5$)+Li$_2$S glass–ceramic. Results suggest that enhancement of the conductivity of the glass–ceramic resulted from improvement of the glass homogeneity. A highly homogeneous glass would decrease the precipitation of LiBr crystal with low conductivity. Low conductivity was obtained for the (Li$_2$S+P$_2$S$_5$)+LiBr glass–ceramic. The (Li$_2$S+P$_2$S$_5$)+LiBr glass–ceramic showed XRD peaks of LiBr crystal with a large intensity as portrayed in Fig. 3-7. Therefore, the growth of LiBr crystal would decrease the conductivity of the (Li$_2$S+P$_2$S$_5$)+LiBr glass–ceramic. The lowest conductivity of the (Li$_2$S+LiBr)+P$_2$S$_5$ glass–ceramic would result from the degradation of the crystallinity of the Li$_7$P$_3$S$_{11}$ crystal and the precipitation of Li$_2$S crystal, as portrayed in Fig. 3-7. To obtain high conductivity for the 90(0.7Li$_2$S·0.3P$_2$S$_5$)·10LiBr glass–ceramic, P$_2$S$_5$ as a network former of the glass should be mixed from the beginning of the vitrification process. The milling period of time for the vitrification should also be controlled to enhance the glass–ceramic conductivity, because the precipitation of LiBr crystal by heat treatment is affected by the milling period of time for the preparation of glasses.

The 90(0.7Li$_2$S·0.3P$_2$S$_5$)·10LiBr glass–ceramic (20hMM) was used in the cells for cyclic voltammetry and charge–discharge measurement. Fig. 3-8 shows the cyclic voltammogram of the glass–ceramic. Large cathodic and anodic currents attributable to deposition and dissolution of lithium metal were observed in the potential range form −0.1 to +0.1 V vs. Li$^+$/Li. The glass–ceramic electrolyte exhibited a wide electrochemical window, because no obvious cathodic or anodic
current was observed up to 10 V. Reportedly, the electrochemical stability range of 67Li2S·33P2S5 glass added with LiI was about 2.9 V vs. Li+/Li [20]. On the other hand, 80(0.7Li2S·0.3P2S5)·20LiI glass exhibited a wide electrochemical stability up to 10 V vs. Li+/Li as demonstrated in Chapter 2. The present study confirmed the high electrochemical stability of the 90(0.7Li2S·0.3P2S5)·10LiBr glass–ceramic.

An all-solid-state cell using the 90(0.7Li2S·0.3P2S5)·10LiBr glass–ceramic electrolyte was fabricated. The charge–discharge curves of the all-solid-state cell are shown in Fig. 3-9. The cell was charged up to 3.6 V vs. Li–In and was discharged to 2.0 V vs. Li–In at the current density of 0.064 mA cm\(^{-2}\). The cell showed an average voltage plateau at 3.3 V in both charge and discharge processes. The cell voltage of 3.3 V vs. Li–In corresponds to the potential of 3.9 V vs. Li+/Li, which is the charge–discharge potential of LiCoO2. The discharge capacity of 90 mAh g\(^{-1}\) was obtained at the first cycle. Coulombic efficiencies of greater than 95 % were obtained except for the first cycle, which indicated that the cell using the 90(0.7Li2S·0.3P2S5)·10LiBr glass–ceramic electrolyte operated as a lithium secondary battery at room temperature. The capacity was decreased gradually with charge–discharge cycling. Decrease of the capacity with cycling was also observed for the cell using the 70Li2S·30P2S5 glass–ceramic electrolyte without LiBr. Consequently, the added LiBr would not decrease the capacity. Results of TEM-EDX analysis indicated that sulfur and phosphorus in the electrolyte added to the composite electrode diffused to the LiCoO2 active material [21]. The diffusion increased the interfacial resistances between the electrolyte and LiCoO2 with cycling. The cycle performance of the cell would be improved using adequate active materials for the electrolyte [22]. The 90(0.7Li2S·0.3P2S5)·10LiBr glass–ceramic material with a high lithium ion conductivity is attractive as a solid electrolyte for a separator layer in all-solid-state batteries.
Table 3-1  Conductivities at 25 °C for the 90(0.7Li$_2$S·0.3P$_2$S$_5$)·10LiBr glasses and glass-ceramics prepared using various milling processes and subsequent heat treatment. The samples labeled as “10hMM”, “20hMM” and “30hMM” were milled for, respectively, 10, 20, and 30 hr. The samples labeled as “(Li$_2$S+P$_2$S$_5$)+LiBr”, “(LiBr+P$_2$S$_5$)+Li$_2$S” and “(Li$_2$S+LiBr)+P$_2$S$_5$” were milled by the two-step milling.

<table>
<thead>
<tr>
<th>Preparation conditions for 90(0.7Li$_2$S·0.3P$_2$S$_5$)·10LiBr (mol%) samples</th>
<th>Conductivity / S cm$^{-1}$</th>
</tr>
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<tbody>
<tr>
<td>Sample</td>
<td>Milling time</td>
</tr>
<tr>
<td>(Li$_2$S+LiBr)+P$_2$S$_5$</td>
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<tr>
<td>(LiBr+P$_2$S$_5$)+Li$_2$S</td>
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</table>
Fig. 3-1 XRD patterns of the $(100-x)(0.7Li_2S\cdot0.3P_2S_5)\cdot xLiBr$ samples prepared by milling for 10 hr.
Fig. 3-2 DTA curves of the (100−x)(0.7Li2S·0.3P2S5)·xLiBr samples prepared by milling for 10 hr.
Fig. 3-3 XRD patterns of the \((100-x)(0.7\text{Li}_2\text{S}-0.3\text{P}_2\text{S}_5)\cdot x\text{LiBr}\) glass-ceramics prepared by milling for 10 hr and subsequent heat treatment.
Fig. 3-4 Composition dependence of conductivities at 25 °C for the (100–x)(0.7Li$_2$S·0.3P$_2$S$_5$)·xLiBr glasses and glass–ceramics prepared by milling for 10 hr and subsequent heat treatment.
Fig. 3-5 XRD patterns of the 90(0.7Li\textsubscript{2}S\cdot0.3P\textsubscript{2}S\textsubscript{5})\cdot10LiBr glasses prepared using various milling processes. The samples labeled as “10hMM”, “20hMM” and “30hMM” were milled for, respectively, 10, 20, and 30 hr. The samples labeled as “(Li\textsubscript{2}S+P\textsubscript{2}S\textsubscript{5})+LiBr”, “(LiBr+P\textsubscript{2}S\textsubscript{5})+Li\textsubscript{2}S” and “(Li\textsubscript{2}S+LiBr)+P\textsubscript{2}S\textsubscript{5}” were milled by the two-step milling.
Fig. 3-6 DTA curves of the 90(0.7Li₂S·0.3P₂S₅)·10LiBr glasses prepared using various milling processes.
Fig. 3-7 XRD patterns of the 90(0.7Li₂S·0.3P₂S₅)·10LiBr glass-ceramics prepared using various milling processes and subsequent heat treatment.
Fig. 3-8 Cyclic voltammogram of the 90(0.7Li$_2$S·0.3P$_2$S$_5$)·10LiBr glass-ceramic electrolyte. The scan rate was 5 mV s$^{-1}$. The potential was swept between $-0.1$ and +10 V.
Fig. 3-9 Charge–discharge curves of the all-solid-state cell
In/90(0.7Li₂S-0.3P₂S₅)-10LiBr glass-ceramic/LiCoO₂ at 25 °C. The cell was charged and discharged between 2.0 V and 3.6 V at the current density of 0.064 mA cm⁻².
3-4. Summary

New electrolytes of \((100-x)(0.7\text{Li}_2\text{S} \cdot 0.3\text{P}_2\text{S}_5)x\text{LiBr}\) \((x = 0, 5, 10, 12.5, 15\) and 20\) were synthesized. Glass electrolytes were obtained by mechanical milling in the composition range of \(x = 0\) to 20. The glass conductivity increased concomitantly with increasing LiBr content. The glass at \(x = 20\) showed conductivity of \(3.1 \times 10^{-4}\) S cm\(^{-1}\). Glass–ceramic electrolytes were prepared using heat treatment for the glasses. The \(\text{Li}_7\text{P}_3\text{S}_{11}\) crystals with high lithium ion conductivity and LiBr crystals were precipitated in all glass–ceramic electrolytes with added LiBr. High conductivity of \(6.4 \times 10^{-3}\) S cm\(^{-1}\) was obtained at \(x = 10\). Furthermore, the conductivity of the \(90(0.7\text{Li}_2\text{S} \cdot 0.3\text{P}_2\text{S}_5)\cdot 10\text{LiBr}\) glass–ceramic electrolyte was improved to \(8.4 \times 10^{-3}\) S cm\(^{-1}\) by controlling of the milling period used to prepare the precursor glass. The \(90(0.7\text{Li}_2\text{S} \cdot 0.3\text{P}_2\text{S}_5)\cdot 10\text{LiBr}\) glass–ceramic electrolyte showed a wide electrochemical window up to 10 V and functioned as an electrolyte for an all-solid-state lithium secondary battery.
3-5. References

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4. Characterization of 70Li$_2$S·30P$_2$S$_5$ glass-ceramic electrolytes with lithium halides

4-1. Introduction

Lithium ion batteries with high energy density are important components of portable electronic equipment such as mobile phones and laptop computers. Large capacity cells are also put into practical use and are adopted as power supplies for electric vehicles. Large cells are anticipated for use in electric power grids with the aim of power storage and load-frequency control. The high energy density of lithium ion batteries is attributable to the high voltage of the cells. Liquid electrolytes containing organic solvents are used in lithium ion batteries because they are stable under the high voltage of the cells. However, organic electrolytes pose a risk of combustion because of their flammability. All-solid-state lithium batteries using solid electrolytes are anticipated to resolve persistent safety problems.

Non-flammable inorganic electrolytes, especially oxide and sulfide glasses and glass-ceramics, are attractive as electrolytes of all-solid-state lithium batteries because they show high lithium ion conductivity [1–14]. Oxide glasses in the binary Li$_2$O–B$_2$O$_3$ system synthesized by melt quenching have low conductivity of 10$^{-7}$ S cm$^{-1}$ at room temperature [1]. However, the addition of lithium halides to the glasses increases their conductivity. Ternary glass of 23Li$_2$O·42B$_2$O$_3$·35LiCl (mol%) shows conductivity of 10$^{-6}$ S cm$^{-1}$ at room temperature [2]. The conductivity increases concomitantly with increasing lithium halide content. Given equal lithium halide contents, the larger the size of halide ion is, the higher the conductivity is. Sulfide glasses in the binary Li$_2$S–B$_2$S$_3$ system synthesized by melt
Incorporation of LiI into the Li$_2$S–B$_2$S$_3$ glasses enhances conductivity up to $1.7 \times 10^{-3}$ S cm$^{-1}$ at the composition of 30Li$_2$S·26B$_2$S$_3$·44LiI [3]. Glasses in the Li$_2$S–SiS$_2$ system also have conductivity of $10^{-4}$ S cm$^{-1}$ at room temperature [5–7]. The conductivity of Li$_2$S–SiS$_2$ glasses is increased by the addition of lithium halides. The conductivity of the glasses added with LiI is higher than that of glasses added with LiBr of the same concentration [5]. In fact, 42Li$_2$S·28SiS$_2$·30LiI glass has conductivity of $1.8 \times 10^{-3}$ S cm$^{-1}$ [6]. Glasses in the Li$_2$S–P$_2$S$_5$ system prepared by melt quenching have conductivity of $10^{-4}$ S cm$^{-1}$ at room temperature [4, 8, 9]. The addition of LiI to Li$_2$S–P$_2$S$_5$ glasses enhances conductivity just as it does with the other glasses. 37Li$_2$S·18P$_2$S$_5$·45LiI glass shows conductivity of $1 \times 10^{-3}$ S cm$^{-1}$ [8, 9]. The Li$_2$S–P$_2$S$_5$ glasses are synthesized by mechanical milling [10]. The Li$_2$S–P$_2$S$_5$ glasses obtained by mechanical milling show roughly equal conductivities of melt-quenched glasses. In addition, the glass-forming range achieved by mechanical milling is extended to higher Li$_2$S contents than that by melt quenching. Sulfide glass–ceramics in the Li$_2$S–P$_2$S$_5$ system were prepared by crystallization of the milled glasses [11–13]. Crystal phases precipitated from the Li$_2$S–P$_2$S$_5$ glasses differ depending on the composition. The 80Li$_2$S·20P$_2$S$_5$ glass–ceramic, which has a thio-LISICON II analog phase as a primary crystal, shows conductivity of $1.3 \times 10^{-3}$ S cm$^{-1}$ at 25 °C [12, 13]. The 75Li$_2$S·25P$_2$S$_5$ glass–ceramic has a thio-LISICON III analog phase and conductivity of $3.2 \times 10^{-4}$ S cm$^{-1}$ [12, 13]. The 70Li$_2$S·30P$_2$S$_5$ glass–ceramic containing Li$_3$P$_2$S$_3$ crystal has high conductivity of $5.2 \times 10^{-3}$ S cm$^{-1}$ [14, 15]. As sulfide crystals containing halide, lithium argyrodites of Li$_6$PS$_3$I, Li$_6$PS$_3$Br, and Li$_6$PS$_3$Cl were synthesized [16, 17]. Li$_6$PS$_3$Cl showed high conductivity of $1.3 \times 10^{-3}$ S cm$^{-1}$.

As described above, incorporation of lithium halides into binary glasses is
effective for enhancing the lithium ion conductivity. Conductivities depending on added lithium halides were investigated for Li$_2$O–B$_2$O$_3$ and Li$_2$S–SiS$_2$ glasses. The influence of added LiI on the conductivity was studied for Li$_2$S–P$_2$S$_5$ glass. However, the influence of other lithium halides has not been clarified for Li$_2$S–P$_2$S$_5$ glass. Moreover, the conductivities and structures of Li$_2$S–P$_2$S$_5$ glass–ceramics added with lithium halides have not been investigated. Therefore, Li$_2$S–P$_2$S$_5$ glasses and glass–ceramics added with lithium halides are focused in this study. The detailed properties of Li$_2$S–P$_2$S$_5$–LiI and Li$_2$S–P$_2$S$_5$–LiBr glasses and glass–ceramics are discussed in Chapters 2 and 3.

In this study, conductivities and structures depending on added lithium halides were discussed for ternary glasses and glass–ceramics of 70Li$_2$S·30P$_2$S$_5$ added with LiF, LiCl, LiBr, and LiI. The composition of 70Li$_2$S·30P$_2$S$_5$ was selected because glass–ceramic of 70Li$_2$S·30P$_2$S$_5$ has the highest conductivity in the binary Li$_2$S–P$_2$S$_5$ system. The ternary glasses and glass–ceramics were prepared. Their conductivities and crystalline phases were examined. The differences of the properties were discussed from the viewpoint of added halides.
4-2. Experimental

4-2-1. Sample preparation

\[(100-y)(0.7\text{Li}_2\text{S} \cdot 0.3\text{P}_2\text{S}_5)\cdot y\text{Li}X \text{ (mol\%)} \ (0 \leq y \leq 20, \ X = \text{F, Cl, Br, and I})\] glasses were obtained by mechanical milling. Reagent-grade \text{Li}_2\text{S} (99.9\%; Nippon Chemical Industrial Co.), \text{P}_2\text{S}_5 (99\%; Aldrich), \text{LiF} (99.99\%; Aldrich), \text{LiCl} (99.998\%; Aldrich), \text{LiBr} (99.999\%; Aldrich), and \text{LiI} (99.99\%; Aldrich) were used as starting materials. They were mixed in an agate mortar for 10 min and put into a 45 ml \text{ZrO}_2\) pot with 500 4-mm-diameter \text{ZrO}_2\) balls. The pot was set in a planetary ball mill apparatus (Pulverisette 7; Fritsch GmbH). Then mechanical milling was performed at 500 rpm for 10 hr. All processes were conducted in a dry \text{Ar} atmosphere. Glass-ceramic samples were prepared by heating the glass samples.

4-2-2. Characterization

Differential thermal analyses (DTA) were performed using a thermal analyzer (Thermo-plus 8120; Rigaku Corp.) to observe crystallization temperatures. The glass samples, which were sealed in Al pans in an \text{Ar}-filled glove box, were heated at 10 °C min\(^{-1}\) under \text{N}_2\) gas flow up to 400 °C. X-ray diffraction (XRD) measurements (\text{CuK}\alpha\) were conducted using a diffractometer (SmartLab; Rigaku Corp.) to identify crystal phases of the glass samples and the glass-ceramic samples. Ionic conductivities were measured for the pelletized samples pressed under 360 MPa. The pellet diameter and thickness were, respectively, 10 mm and about 1.5 mm. Carbon paste was painted as electrodes on both faces of the pellets. Then stainless steel disks were attached to the pellets as current collectors. The prepared cell was sealed in a silica glass tube. Then AC impedance measurements were conducted under dry \text{Ar} gas flow using an impedance analyzer (1260; Solartron). The frequency range and the applied voltage were, respectively, 10 Hz to 8 MHz and
50 mV. The AC impedance measurements were conducted at 25 °C for the glass samples. Then the pellets were heated to above the crystallization temperatures to obtain glass-ceramics. The impedances of glass-ceramic samples were measured after cooling the pellets to 25 °C.
4-3. Results and discussion

Figs. 4-1 and 4-2 respectively portray XRD patterns of the 90(0.7Li$_2$S·0.3P$_2$S$_5$)·10LiX and 80(0.7Li$_2$S·0.3P$_2$S$_5$)·20LiX samples (X = F, Cl, Br, and I) prepared using mechanical milling. The XRD pattern of 70Li$_2$S·30P$_2$S$_5$ is also depicted in the figures. Halo patterns were observed for all samples. A weak diffraction peak attributable to LiF crystals remained in the XRD patterns of the 90(0.7Li$_2$S·0.3P$_2$S$_5$)·10LiF and 80(0.7Li$_2$S·0.3P$_2$S$_5$)·20LiF samples. Weak diffraction peaks attributable to LiCl crystals were observed in the XRD patterns of the 80(0.7Li$_2$S·0.3P$_2$S$_5$)·20LiCl sample. No crystal peak remained in the milled samples of X = Br and I. All the milled samples had amorphous phase. Nevertheless, obtaining fully amorphous phase without residues of LiF and LiCl was difficult, even after prolonged milling time.

The DTA curves of the 90(0.7Li$_2$S·0.3P$_2$S$_5$)·10LiX and 80(0.7Li$_2$S·0.3P$_2$S$_5$)·20LiX samples (X = F, Cl, Br, and I) prepared by mechanical milling are presented in Figs. 4-3 and 4-4. The DTA curve of 70Li$_2$S·30P$_2$S$_5$ is also shown in the figures. Glass transition phenomena occurred between 175 °C and 220°C, indicating that the amorphous phases obtained by mechanical milling were glasses. Exothermic peaks were observed between 230 °C and 270°C. These exothermic peaks resulted from glass crystallization because the samples heated to temperatures that were slightly above these temperatures exhibited crystalline XRD pattern as shown in Figs. 4-5 and 4-6. The glass transition temperatures (Tg) and the crystallization temperatures (Tc) of glasses added with lithium halides were lower than those of the 70Li$_2$S·30P$_2$S$_5$ glass. The Tg of the glasses decreased with increased size of halide ion. Incorporation of larger halide ions with higher polarizability can be expected to decrease the cohesive energy of the glasses, resulting in the decrease of Tg. Tg and Tc shifted to the lower temperature side with
increasing lithium halide content, as portrayed in Fig. 4-4.

The XRD patterns of the 90(0.7Li$_2$S·0.3P$_2$S$_5$)·10LiX and 80(0.7Li$_2$S·0.3P$_2$S$_5$)·20LiX samples prepared using heat treatment are portrayed respectively in Figs. 4-5 and 4-6. The XRD pattern of 70Li$_2$S·30P$_2$S$_5$ is depicted in those figures as well. Several diffraction peaks were observed, indicating that crystals were precipitated in the samples and that glass-ceramics were obtained. All glass-ceramics had Li$_7$P$_3$S$_{11}$ crystals [12]. No marked shift of the peaks attributable to Li$_7$P$_3$S$_{11}$ crystal was observed by addition of LiX. The intensity of the peaks of Li$_7$P$_3$S$_{11}$ crystals was weakened in the 80(0.7Li$_2$S·0.3P$_2$S$_5$)·20LiX glass-ceramic samples, indicating that the Li$_7$P$_3$S$_{11}$ crystal crystallinity was degraded with increased lithium halide content. The peaks attributable to LiF and LiCl crystals were observed respectively in the glass-ceramics added with LiF and LiCl. The precursor glasses partially included LiF and LiCl crystals, as shown in Figs. 4-1 and 4-2. However, the diffraction peaks attributable to LiBr and LiI crystals were observed, respectively, in the glass-ceramics added with LiBr and LiI, although these crystals disappeared in the precursor glasses. These crystals were precipitated through heat treatment. The intensity of the peaks attributable to LiBr crystal was particularly high. The LiBr crystal peak at 28.1 ° in the 90(0.7Li$_2$S·0.3P$_2$S$_5$)·10LiBr glass-ceramic sample showed asymmetric broadening to a larger angle side. The asymmetric broadening of the peak would result from stacking faults on the (111) planes in face-centered cubic structure of LiBr crystals, as described in Chapter 3. No marked asymmetric broadening of the peak was observed in the XRD pattern of the 80(0.7Li$_2$S·0.3P$_2$S$_5$)·20LiBr glass-ceramic. The intensity of the diffraction peaks of LiBr crystals increased, indicating improvement of the LiBr crystallinity. Large unknown peaks were observed in the 90(0.7Li$_2$S·0.3P$_2$S$_5$)·10LiI glass-ceramic. In the 80(0.7Li$_2$S·0.3P$_2$S$_5$)·20LiI, Li$_7$P$_3$S$_{11}$
crystal almost disappeared. The unknown peaks were dominant.

The composition dependence of electrical conductivities at 25 °C for the (100−y)(0.7Li₂S·0.3P₂S₃)·yLiX glasses and glass-ceramics is depicted in Fig. 4-7. The conductivities of the glasses showed monotonous changes in the order of 10⁻⁴ S cm⁻¹. The conductivities of the (100−y)(0.7Li₂S·0.3P₂S₃)·yLiF glasses decreased concomitantly with increasing LiF content. The LiF crystals remaining in the glasses, as shown in Figs. 4-1 and 4-2, cause the degradation of conductivities against increasing of Li⁺ ion content. The (100−y)(0.7Li₂S·0.3P₂S₃)·yLiCl glasses showed almost identical conductivity in the composition range of y = 0 to 20. The conductivities of the (100−y)(0.7Li₂S·0.3P₂S₃)·yLiBr and (100−y)(0.7Li₂S·0.3P₂S₃)·yLiI glasses increased concomitantly with increasing lithium halide content. Two factors increase conductivity: increased Li⁺ ion content and a lack of residues of lithium halide crystals in the glasses. Conductivities of the (100−y)(0.7Li₂S·0.3P₂S₃)·yLiX glass-ceramics showed different changes depending on added lithium halides. The conductivities of (100−y)(0.7Li₂S·0.3P₂S₃)·yLiF glass-ceramic were about 4 × 10⁻³ S cm⁻¹. They only changed slightly in the composition range of y = 0 to 20. Precipitation of Li₇P₃S₁₁ crystals with high conductivity provided equivalent conductivities. For the (100−y)(0.7Li₂S·0.3P₂S₃)·yLiCl glass-ceramics, the conductivities increased slightly along with increasing LiCl content in the composition range of y = 0 to 10. Then the conductivities decreased in the composition range of y = 10 to 20. In the composition range of y = 0 to 10, precipitation of Li₇P₃S₁₁ crystals can be expected to maintain the high conductivities. However, the degradation of crystallinity of Li₇P₃S₁₁ phase can be expected to decrease the conductivities of y = 10 to 20. The conductivities of the (100−y)(0.7Li₂S·0.3P₂S₃)·yLiBr glass-ceramics were enhanced with increasing LiBr content in the composition range of y = 0 to 10. The highest conductivity of 6.5
\( \times 10^{-3} \) S cm\(^{-1}\) was obtained at \( y = 10 \). The increased conductivity is attributable to three factors: precipitation of the Li\(_{7}\)P\(_3\)S\(_{11}\) crystals, increased Li\(^+\) ion content, and high conductivities of the glasses remaining in the glass-ceramics. The precipitation of LiBr crystal is generally regarded as decreasing the conductivities of glass-ceramics because of its low conductivity [18]. However, the LiBr crystal containing stacking faults in its structure might not decrease the conductivities excessively, as described in Chapter 3. The conductivities of the (100\(\times\)y)(0.7Li\(_2\)S\(\cdot\)0.3P\(_2\)S\(_5\))\(\cdot\)yLiBr glass-ceramics decreased concomitantly with increasing LiBr content in the composition range of \( y = 10 \) to 20. The decrease of conductivities is attributable to the degradation of crystallinity of Li\(_{7}\)P\(_3\)S\(_{11}\) phase and to the improvement of crystallinity of LiBr phase. The conductivities of (100\(\times\)y)(0.7Li\(_2\)S\(\cdot\)0.3P\(_2\)S\(_5\))\(\cdot\)yLiI glass-ceramics decreased sharply by the addition of LiI. Precipitation of the unknown phase shown in Figs. 4-5 and 4-6 strongly degraded the conductivity.

Fig. 4-8 presents conductivities at 25 °C for the 90(0.7Li\(_2\)S\(\cdot\)0.3P\(_2\)S\(_5\))\(\cdot\)10LiX glasses and glass-ceramics shown as a function of effective ionic radius of the added halide ion [19]. The conductivities of the 70Li\(_2\)S\(\cdot\)30P\(_2\)S\(_5\) glass and glass-ceramic are also shown. These two conductivities are shown for the ionic radius of S\(^2-\) ion because S\(^2-\) ions as well as halide ions play a role as a counter anion for Li\(^+\) cations. The halide glass conductivity is usually correlated with the polarizability of halide ions. However, it is difficult to estimate polarizability in the glass structure. The conductivities of the 90(0.7Li\(_2\)S\(\cdot\)0.3P\(_2\)S\(_5\))\(\cdot\)10LiX glasses increased concomitantly with the increasing ionic radius of added halide ions. The conductivity of the 70Li\(_2\)S\(\cdot\)30P\(_2\)S\(_5\) glass shown at the ionic radius of S\(^2-\) ion was also on the line. Results suggest that the radii of S\(^2-\) ion and added halide ions affected the glass conductivity. Larger halide ions with higher polarizability can be expected to increase the
conductivities of the 90(0.7Li$_2$S·0.3P$_2$S$_5$)·10LiX glasses in the composition range of \( y = 0 \) to 20. Conductivities of the 90(0.7Li$_2$S·0.3P$_2$S$_5$)·10LiX glass-ceramics except X = I changed in an almost identical manner as the corresponding mother glasses. However, it is unreasonable to explain the conductivities from the viewpoint of the ionic radii of halide ions because the glass-ceramics have different crystalline phases and crystallinities. The ionic radii of added halide ions are anticipated as one factor affecting the precipitated crystals in the glass-ceramics.
Fig. 4-1 XRD patterns of the $90(0.7\text{Li}_2\text{S} \cdot 0.3\text{P}_2\text{S}_5) \cdot 10\text{LiX}$ samples prepared using mechanical milling, and of the $70\text{Li}_2\text{S} \cdot 30\text{P}_2\text{S}_5$ glass.
Fig. 4-2 XRD patterns of the $80(0.7\text{Li}_2\text{S}-0.3\text{P}_2\text{S}_5)-20\text{LiX}$ samples prepared using mechanical milling, and of the $70\text{Li}_2\text{S}-0.3\text{P}_2\text{S}_5$ glass.
Fig. 4–3 DTA curves of the 90(0.7Li₂S·0.3P₂S₅)·10LiX samples prepared using mechanical milling, and of the 70Li₂S·0.3P₂S₅ glass.
Fig. 4-4 DTA curves of the 80(0.7Li₂S·0.3P₂S₅)·20LiX samples prepared using mechanical milling, and of the 70Li₂S·0.3P₂S₅ glass.
Fig. 4-5 XRD patterns of the 90(0.7Li$_2$S·0.3P$_2$S$_5$)-10LiX samples prepared using heat treatment, and of the 70Li$_2$S·30P$_2$S$_5$ glass-ceramic.
Fig. 4-6 XRD patterns of the 80(0.7Li\(_2\)S\(_2\)·0.3P\(_2\)S\(_5\))·20LiX samples prepared using heat treatment, and of the 70Li\(_2\)S·30P\(_2\)S\(_5\) glass-ceramic.
Fig.4-7 Composition dependence of electrical conductivities at 25 °C for the (100−y)(0.7Li₂S·0.3P₂S₅)·yLiX glasses and glass-ceramics.
Fig. 4-8 Conductivities at 25 °C for the 90(0.7Li₂S·0.3P₂S₅)·10LiX glasses and glass-ceramics, shown as a function of effective ionic radius of added halide ion. Conductivities for the 70Li₂S·30P₂S₅ glass and glass-ceramic are also shown for the ionic radius of S²⁻ ion.
4-4. Summary

Glasses of \((100-y)(0.7\text{Li}_2\text{S} \cdot 0.3\text{P}_2\text{S}_5) \cdot y\text{Li}X\) (mol\%) \((0 \leq y \leq 20, X = F, \text{Cl}, \text{Br},\) and \(I)\) were synthesized using mechanical milling. Then glass-ceramics were prepared using heat treatment. The LiF or LiCl crystals slightly remained in the glasses of \(X = F\) or Cl. The glass-ceramics had crystal phases of \(\text{Li}_7\text{P}_3\text{S}_{11}\) and \(\text{LiX}\). The crystallinity of \(\text{Li}_7\text{P}_3\text{S}_{11}\) phase decreased with increasing lithium halide content at nominal composition. The conductivity of the glasses added with LiBr and LiI increased concomitantly with increasing lithium halide contents. The larger ionic radius of halide ions is effective in increasing conductivity of the glasses. The glass-ceramic conductivities showed different changes depending on the added lithium halides. The highest conductivity of \(6.5 \times 10^{-3}\) S cm\(^{-1}\) was obtained for \(70\text{Li}_2\text{S} \cdot 30\text{P}_2\text{S}_5\) glass-ceramic added with LiBr.
4-5. References


5. General Conclusions

In this thesis, enhancement of conductivity for Li$_2$S–P$_2$S$_5$ glass-ceramic electrolytes was investigated by incorporation of lithium halides into the glass-ceramics. The precursor glasses of Li$_2$S–P$_2$S$_5$–LiX (X = F, Cl, Br and I) were prepared by mechanical milling using a planetary ball mill apparatus. Li$_2$S–P$_2$S$_5$–LiX glass-ceramics were obtained by heating the glasses at just above crystallization temperatures. Effects of the addition of lithium halides on the structure, ionic conductivity and electrochemical stability of the glasses and the glass-ceramics were examined. The following results and considerations were obtained.

1. Incorporation of LiI and LiBr into 70Li$_2$S·30P$_2$S$_5$ glass was effective for enhancing the conductivity. The conductivities of the glasses were enhanced with increasing the LiI and LiBr contents. On the other hand, incorporation of LiF into 70Li$_2$S·30P$_2$S$_5$ glass decreased the conductivity. Incorporation of LiCl into 70Li$_2$S·30P$_2$S$_5$ glass had almost no effect on the conductivity. Higher polarizability of larger halide ions would increase the conductivities of the glasses. The highest conductivity of $5.6 \times 10^{-4}$ S cm$^{-1}$ was obtained for the 80(0.7Li$_2$S·0.3P$_2$S$_5$)·20LiI glass. The 80(0.7Li$_2$S·0.3P$_2$S$_5$)·20LiI glass exhibited a wide electrochemical stability up to 10 V vs. Li$^+$/Li.

2. Incorporation of lithium halides into 70Li$_2$S·30P$_2$S$_5$ glass-ceramic affected the crystal phases precipitated in the glass-ceramics. All the glass-ceramics contained Li$_7$P$_3$S$_{11}$ crystals. Substitution of halide ions into the Li$_7$P$_3$S$_{11}$ crystals was not observed. The crystallinity of Li$_7$P$_3$S$_{11}$ crystals was degraded with increasing the
lithium halide content. The 70Li₂S·30P₂S₅ glass-ceramics added with LiI contained unknown crystals. The unknown phase became dominant with increasing the LiI content. The 70Li₂S·30P₂S₅ glass-ceramics added with LiBr showed marked precipitation of LiBr crystals. The precipitated LiBr crystals were considered to have stacking faults on the (111) planes in face-centered cubic structure. The 70Li₂S·30P₂S₅ glass-ceramics added with LiF, LiCl, and LiI, respectively, showed weak XRD peaks attributable to LiF, LiCl, and LiI.

3 The conductivities of 70Li₂S·30P₂S₅ glass-ceramic were changed by the addition of lithium halides. The addition of LiI to the 70Li₂S·30P₂S₅ glass-ceramic dramatically decreased the conductivity. It was suggested that the precipitation of the unknown phase decreased the conductivity. The addition of LiBr to the 70Li₂S·30P₂S₅ glass-ceramic was effective for enhancing the conductivity in the composition range up to 10 mol% of LiBr. However, the conductivity was decreased in the composition range over 10 mol%. The conductivities of the 70Li₂S·30P₂S₅ glass-ceramics added with LiCl changed in the same manner as the glass-ceramics added with LiBr. The addition of LiF to the 70Li₂S·30P₂S₅ glass-ceramic had almost no effect on the conductivity for the composition range up to 20 mol% of LiF. The highest conductivity of 6.5 × 10⁻³ S cm⁻¹ was obtained for the 90(0.7Li₂S·0.3P₂S₅)·10LiBr glass-ceramic.

4 The milling period used to prepare the precursor glasses affected the conductivities of glass-ceramics. The conductivity of 6.5 × 10⁻³ S cm⁻¹ for the 90(0.7Li₂S·0.3P₂S₅)·10LiBr glass-ceramic was increased to 8.0 × 10⁻³ S cm⁻¹ by prolonging the milling period from 10 hr to 20 hr. The crystallinity of LiBr crystals was degraded in the glass-ceramic obtained from the 20 hr milling glass. It was
suggested that improvement of the glass homogeneity inhibited the precipitation of LiBr crystals, resulting in enhancement of the conductivity. The 90(0.7Li$_2$S·0.3P$_2$S$_5$)·10LiBr glass-ceramic had a wide electrochemical stability up to 10 V vs. Li$^+$/Li. An all-solid-state lithium secondary battery using 90(0.7Li$_2$S·0.3P$_2$S$_5$)·10LiBr glass-ceramic as an electrolyte was charged and discharged successfully.

5 Incorporation of LiI into 80Li$_2$S·20P$_2$S$_5$ glass was effective for enhancing the conductivity. The conductivities of the glass were enhanced with increasing the LiI content. The highest conductivity of 6.5 × 10$^{-3}$ S cm$^{-1}$ was obtained for the 80(0.8Li$_2$S·0.2P$_2$S$_5$)·20LiI glass.

6 Incorporation of LiI into 80Li$_2$S·20P$_2$S$_5$ glass-ceramic affected the crystal phases precipitated in the glass-ceramics. The thio-LISICON III analog phase was mainly precipitated in the 80Li$_2$S·20P$_2$S$_5$ glass-ceramic, and the thio-LISICON II analog phase was mainly precipitated in the glass-ceramics added with LiI. The glass-ceramic of 95(0.8Li$_2$S·0.2P$_2$S$_5$)·5LiI with the highest conductivity of 2.7 × 10$^{-3}$ S cm$^{-1}$ showed a wide electrochemical window of about 10 V vs. Li$^+$/Li. The addition of LiI to the 80Li$_2$S·20P$_2$S$_5$ glass was effective for precipitation of the thio-LISICON II analog phase with high conductivity.
List of publications

Original articles regarding this study are as follows:

1. “Structure, ionic conductivity and electrochemical stability of Li₂P₂S₅-LiI glass and glass-ceramic electrolytes”
   S. Ujiie, A. Hayashi and M. Tatsumisago,
   Solid State Ionics 211 (2012) 42. (Chapter 2)

2. “Preparation and ionic conductivity of (100–x)(0.8Li₂S-0.2P₂S₅)-xLiI glass-ceramic electrolytes”
   S. Ujiie, A. Hayashi and M. Tatsumisago,
   J. Solid State Electrochem. 17 (2013) 675. (Chapter 2)

3. “Preparation and electrochemical characterization of (100–x)(0.7Li₂S-0.3P₂S₅)-xLiBr glass-ceramic electrolytes”
   S. Ujiie, A. Hayashi and M. Tatsumisago,

4. “Structure and conductivity of 70Li₂S·30P₂S₅ glass and glass-ceramic electrolytes added with lithium halides”
   S. Ujiie, T. Inagaki, A. Hayashi and M. Tatsumisago
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