High Lithium Ion Conductivity of Glass–Ceramics Derived from Mechanically Milled Glassy Powders

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Crystallization of the $80Li_2S\cdot20P_2S_5$ (mol%) glassy powders derived from mechanical milling improved their conductivities. The obtained glass–ceramic exhibited high conductivity of approximately 10^{-3} S cm^{-1} at room temperature. The stabilization of the high-temperature phase of Li_7PS_6 crystal in the glass matrix brought about those high conductivities.

Solidification of electrolytes is indispensable to develop the safe and reliable lithium secondary batteries with high energy density. In order to realize solid-state batteries, solid electrolytes with high lithium ion conductivity comparable to liquid electrolytes are strongly desired. Sulfide based glasses prepared by melt-quenching are known to show high lithium ion conductivity over 10^{-4} S cm^{-1} at room temperature.[1–4] These highly conductive glassy materials are also synthesized at room temperature as fine powders by mechanical milling technique using a high-energy ball-mill.[5–7] The fine powders are favorable to achieve close solid/solid contact between solid electrolytes and electrode materials. Mechanical milling is thus a very useful and simple procedure to prepare high lithium ion conducting solid electrolytes.

In the present study, we have found that crystallization of the $80Li_2S\cdot20P_2S_5$ (mol%) glassy powders derived from mechanical milling improves their conductivities. In general, crystallization of glassy materials is well known to lower the conductivities.[8,9] The enhancement of conductivities after crystallization as shown here is the first case in the ion conductive sulfide glassy materials. The obtained glass–ceramics exhibit high conductivities of approximately 10^{-3} S cm^{-1} at room temperature. Here we describe in detail the synthesis method and the characterization of the highly conductive glass–ceramics. The reason why the conductivity improves after crystallization of the glassy powders is also discussed.

Reagent-grade Li_2S (Furuuchi Chem., 99.9%) and P_2S_5 (Koujyundo Chem., 98%) crystalline powders were used as starting materials for sample preparation. The mechanical milling treatment was carried out for the batches (1 g) of the mixed materials at the composition $80Li_2S\cdot20P_2S_5$ (mol%) in an alumina pot (volume = 45 mL) with alumina balls (10 balls with a diameter 10 mm) using a high-energy planetary ball mill (Fritsch Pulverisette 7). The rotation speed was fixed to be 370 rpm and all the processes were carried out at room temperature in a dry N_2-filled glove box ($[H_2O] < 1$ ppm).

X-ray diffraction measurements for the $80Li_2S\cdot20P_2S_5$ powder indicated that the intensity of the diffraction peaks due to Li_2S and P_2S_5 crystals gradually decreased with an increase in milling periods of time. Although the diffraction peaks due to Li_2S crystal were very slightly observed, the $80Li_2S\cdot20P_2S_5$ powder was almost amorphous after mechanical milling for 20 h. Differential thermal analysis revealed that an endothermic behavior due to glass transition and an exothermic peak due to crystallization were observed respectively at 180 and 190 °C in the $80Li_2S\cdot20P_2S_5$ powder mechanically milled for 20 h. Therefore, the amorphous powder is in glassy state. The obtained powder is a few μm in diameter.

The electrical conductivity for the $80Li_2S\cdot20P_2S_5$ powder which was pelletized by cold pressing under a pressure 3700 kg/cm^2 was measured by the AC impedance method in the temperature range 25–250 °C and the frequency range 100 Hz–15 MHz. Only one semicircle due to both bulk and grain-boundary impedance was observed. Figure 1 shows the temperature dependence of electrical conductivity of the $80Li_2S\cdot20P_2S_5$ pelletized sample of the glassy powders mechanically milled for 20 h. Open and closed circles denote the heating and the cooling runs, respectively. The as-prepared glassy sample exhibits high conductivity of 2×10^{-4} S cm^{-1} at room temperature. The conductivity of the glassy sample follows the Arrhenius equation in the heating run. After the sample is heated up to 250 °C, which is beyond the crystallization temperature, the conductivity changes with a different manner in the cooling run. The conductivity of the heated sample is 9×10^{-4} S cm^{-1} at room temperature and this value is extremely high as the pelletized ionic conductor. The activation energies for conduction decrease from 35 kJ mol^{-1} in the heating run to 24 kJ mol^{-1} in the cooling run. The pelletized materials kept high conductivity after further cyclings of heating and cooling runs in the same temperature range.

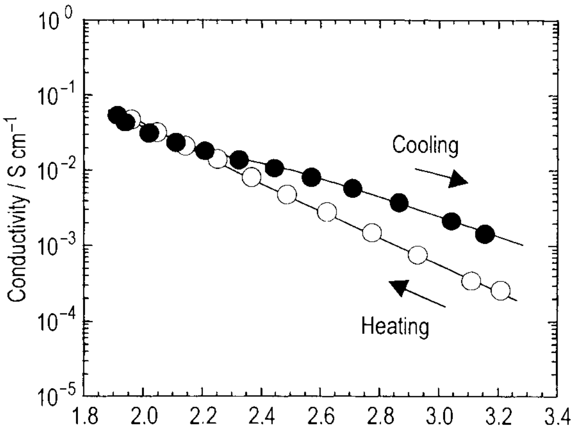

Figure 1. Temperature dependence of electrical conductivities of the $80Li_2S\cdot20P_2S_5$ pelletized samples of powders mechanically milled for 20 h. Open and closed circles denote the heating and cooling runs, respectively.

The obtained materials are glass–ceramics including the crystals in the glass matrix because crystallization must take place in the heating run over the crystallization temperature. In ionic conductors, glasses generally exhibit higher conductivities than corresponding crystals because glasses with random and open structure have larger free volume than crystals;[8,9] the mobility of ions becomes larger with an increase in free volume. Therefore, the enhancement of the conductivity after crystallization is uncommon in the ion conducting materials as shown in Figure 1. We have found this unique phenomenon for the first time in the sulfide lithium ion conducting materials.

The precipitated crystal is expected to have high conductivity because the conductivity of the glass–ceramics sample with the crystal was much higher than that of the corresponding glassy sample. In order to identify the crystal phase, X-ray diffraction measurement was carried out for the glass–ceramics. Figure 2 shows the X-ray diffraction patterns of the $80Li_2S{\cdot}20P_2S_5$ samples at room temperature before and after the conductivity measurements shown in Figure 1. The Li_7PS_6 crystal phase (JCPDS#34-0688) is mainly precipitated in the sample after the conductivity measurements. The conductivity measurements have never been reported so far for the Li_7PS_6 crystal. Then, we synthesized the Li_7PS_6 crystal using a solid-phase reaction and measured its conductivity. The pelletized Li_7PS_6 crystal powders exhibited the conductivity of 8×10^{-5} S cm^{-1} at room temperature; this value is, however, one order of the magnitude lower than the value of the glass–ceramics 9×10^{-4} S cm^{-1}. Then, we presume that the enhancement of the conductivity is due to the crystallization of the high-temperature phase of Li_7PS_6, which must have considerably high conductivity. In the case of crystallization from glassy state, high-temperature crystalline phases are usually crystallized as the first precipitated crystal. It is exemplified by the crystallization of silica glass, which occurs in the temperature range of 1200 to 1400 °C, to form the high-temperature phase cristobalite as the first precipitated crystalline product instead of the thermodynamically stable phase, tridymite.[10] One of the reasons for this is usually found in the structural similarity between the original glass and the precipitated crystal. In general, high-temperature phases have a more open structure than low-temperature crystalline phases and, therefore, are more similar to the structure of a glassy starting material. As a result, high-temperature phases tend to crystallize from the glassy state even in the temperature range where low-temperature phases are thermodynamically stable. Although the structure and properties of the high-temperature phase of Li_7PS_6 crystal have not been clear in the present stage, it can be said that the high-temperature phase is probably stabilized in the sulfide glass matrix by the crystallization of mechanically milled $80Li_2S{\cdot}20P_2S_5$ glassy powder.

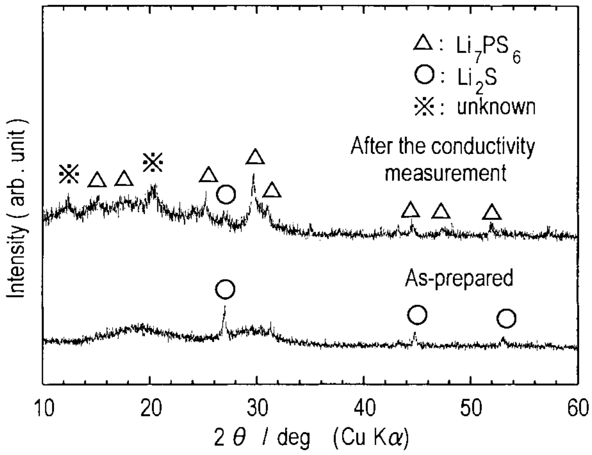

Figure 2. X-ray diffraction patterns of the $80Li_2S{\cdot}20P_2S_5$ samples mechanically milled for 20 h before and after the conductivity measurement as shown in Fig. 1. Open circles and triangles denote Li_2S and Li_7PS_6 crystals, respectively.

The improvement in the contact among glassy powders is also one of the factors of the conductivity enhancement. It was revealed from scanning electron microscope observations that the glass–ceramics have very dense microstructure with no voids among powders. This is because the glassy powders are softened by being heated over the glass transition temperature. The construction of the close contact between solid electrolyte and electrode powders is indispensable to realize the superior solid-state lithium secondary batteries. The softening of the $80Li_2S{\cdot}20P_2S_5$ glassy powder obtained in the present study must form the close solid/solid contact between electrolyte and electrode powders.

In conclusion, we have discovered for the first time that crystallization from the glassy state enhances the conductivity in the sulfide lithium ion conducting materials. The $80Li_2S{\cdot}20P_2S_5$ glass–ceramic prepared by the heat-treatment of the mechanically milled glassy powder exhibited high conductivity of approximately 10^{-3} S cm^{-1} at room temperature. We have discussed the enhancement of the conductivity after crystallization in terms of the stabilization of the high-temperature phase of Li_7PS_6 crystal with high conductivity.

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