Evaluation of elastic modulus of Li$_2$S–P$_2$S$_5$ glassy solid electrolyte by ultrasonic sound velocity measurement and compression test

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Elastic modulus is an important factor of solid electrolytes for an all-solid-state battery as a next-generation battery. In this study, Young’s moduli of dense pellets of the Li$_2$S–P$_2$S$_5$ glass solid electrolytes prepared by room temperature pressing and hot pressing were investigated. The Young’s moduli of Li$_2$S–P$_2$S$_5$ hot-pressed pellets measured by ultrasonic sound velocity measurements were 18–25 GPa and those of cold-pressed pellets were about 14–17 GPa. The compression test was also done to determine Young’s modulus. The Young’s modulus of Li$_2$S–P$_2$S$_5$ glasses increased with increasing the Li$_2$S content in both hot press and cold press pellets. The Young’s moduli were lower than those of oxide based solid electrolytes.

Key-words : Solid electrolyte, Young’s modulus, Elastic modulus, Sulfide glass, All-solidstate battery, Hot press

1. Introduction

There is an increasing demand for large-scale secondary batteries with high safety and energy density for the application to power sources for electric vehicles and energy storage systems for renewable energy. All-solid-state lithium secondary batteries using inorganic solid electrolytes are a potential candidate for next generation batteries with extremely high energy density. Conventional lithium-ion secondary batteries have been widely used as a high energy density battery. However, they contain liquid electrolytes using flammable organic solvents and thus have safety concerns. Improvement of the safety of batteries is expected in all-solid-state batteries by using inorganic solid electrolytes instead of organic liquid electrolytes. The improvement of energy density is also expected in the all-solid-state batteries because high capacity electrode materials such as elemental sulfur and lithium sulfide will be used.

Many challenges should be done for realizing all-solid-state batteries. Mechanical properties of solid electrolytes are important for being developed. For example, solid electrolytes should have high processability to construct intimate solid-solid contacts between electrode active materials and solid electrolytes. The intimate contacts between solid particles are essential to achieve high performance such as high capacity, long cycle life, and high rate capability. Both electrode active materials and electrolytes are solid in the all-solid-state batteries; it is thus difficult to construct the intimate contact between electrode and electrolyte compared to the conventional batteries using liquid electrolytes. Furthermore, the contact should be held during charging and discharging although volume of the electrode active materials changes during charging and discharging. The mechanical properties of electrode and solid electrolytes should affect the electrode/electrolyte contacts during cycling.

Elastic modulus is an important mechanical property to investigate the electrode/electrolyte contact. The understanding of elastic modulus of the solid electrolytes is necessary for the development of new solid electrolytes with suitable mechanical properties for all-solid-state lithium secondary batteries. Some papers report the elastic modulus of lithium-ion conducting oxide solid electrolytes. However, there are few papers which reports elastic modulus of highly conductive sulfide solid electrolytes because of the difficulty of the experiments in air atmosphere.

Sulfide solid electrolytes as the Li$_2$S–P$_2$S$_5$ glasses show lithium-ion high conductivity. The Li$_2$S–P$_2$S$_5$ glasses are potential candidates for solid electrolytes of all-solid-state lithium secondary batteries. Recently, we achieved the preparation of almost fully dense pellets of the Li$_2$S–P$_2$S$_5$ glasses by hot press from the glass powder at around their glass transition temperatures.

The mechanical properties like Young’s modulus as well as electrical properties were varied with the composition in the Li$_2$S–P$_2$S$_5$ glasses. It is important to clarify the relationship between composition and the properties. Furthermore, the electrolytes were used as powder compressed pellets in the bulk-type (powder-type) all-solid-state batteries. Therefore, the investigation of mechanical properties of the compressed pellets as well as fully dense pellets is valuable.

In this paper, the dense pellets of the Li$_2$S–P$_2$S$_5$ system glassy solid electrolytes were prepared by room temperature pressing and hot pressing. Young’s moduli of the prepared dense pellets were investigated by ultrasonic sound velocity measurements and compression tests. The relationship among Young’s modulus of the pellets, the glass composition, applied pressures, and temper-
Electrolytes prepared using various molding pressures and temperatures. The shear modulus, Young's modulus, and Poisson's ratio were calculated using an ultrasonic sound velocity technique. The Li$_2$La$_2$Zr$_2$O$_{12}$ ceramic pellet was prepared by sintering at 1230°C, and the 60KNO$_3$·40Ca(NO$_3$)$_2$ glass pellet was prepared by the melt quenching method.

### Results and discussion

The Young’s moduli of the sulfide glass electrolyte pellets with various compositions, molding temperature and molding pressure were investigated. The Young’s moduli measured using an ultrasonic sound velocity technique were listed in Table 1. The density of 50Li$_2$S·50P$_2$S$_5$ glass prepared in this study (1.89 g cm$^{-3}$) is in good agreement with the density reported for the corresponding glass which was prepared by the melt quenching method, indicating that almost fully dense pellets were obtained by the hot press near 200°C. The Young’s moduli of the Li$_2$S·P$_2$S$_5$ glasses prepared hot and cold pressing at 360 MPa were also shown in Fig. 1. The Young’s moduli of Li$_2$S·P$_2$S$_5$ hot-pressed pellets were 18–25 GPa and those of cold-pressed pellets were about 14–17 GPa. The Young’s moduli of cold-pressed pellets were lower than those of hot-pressed pellets. The Young’s moduli of Li$_2$S·P$_2$S$_5$ glasses increases with increasing the Li$_2$S content in both hot-pressed and cold-pressed pellets. The highly dense pellets tend to be prepared by pressing with high molding temperature and pressure. For example, the densities of 75Li$_2$S·25P$_2$S$_5$ glasses prepared at the pressures of 180 and 360 MPa at room temperature were 1.68, 1.86, 1.89, and 1.88 g cm$^{-3}$, respectively. Those prepared at room temperature, 100, 150 and 190°C at the 360 MPa were respectively 1.68, 1.86, 1.89, and 1.88 g cm$^{-3}$. Almost fully dense pellets were obtained by hot press at temperatures higher than 100°C at 360 MPa. In this study, the Young’s moduli of typical oxide electrolyte Li$_2$La$_2$Zr$_2$O$_{12}$ and ionic glass 60KNO$_3$·40Ca(NO$_3$)$_2$ were also evaluated. The Li$_2$La$_2$Zr$_2$O$_{12}$ ceramic was prepared by normal sintering at a high temperature of 1230°C without pressure. The theoretical density of Li$_2$La$_2$Zr$_2$O$_{12}$ calculated from crystal structure was 5.1 g cm$^{-3}$. The density of the prepared Li$_2$La$_2$Zr$_2$O$_{12}$ pellet was 4.52 g cm$^{-3}$, the relative density was 88%. The Li$_2$La$_2$Zr$_2$O$_{12}$

### Table 1. Velocities of longitudinal and shear waves, density, shear modulus, Young’s modulus, Poisson’s ratio of xLi$_2$S·(100 − x)P$_2$S$_5$ (mol%) solid electrolytes prepared using various molding pressures and temperatures.

| Sample               | Molding temperature /°C | Molding pressure /MPa | Velocity of longitudinal wave $V_L$/m·s$^{-1}$ | Velocity of shear wave $V_S$/m·s$^{-1}$ | Density $\rho$/g·cm$^{-3}$ | Shear modulus $G$/GPa | Young’s modulus $E$/GPa | Poisson’s ratio $\nu$ |
|----------------------|-------------------------|-----------------------|-----------------------------------------------|---------------------------------------|---------------------------|------------------------|--------------------------|------------------------|
| Si$_3$N$_4$           | —                       | —                     | 10.830                                        | 6.050                                 | 3.1                       | 114                    | 289                     | 0.27                   |
| Si$_3$N$_4$ (in polymer pack) | —                       | —                     | 10.770                                        | 6.060                                 | 3.1                       | 114                    | 289                     | 0.27                   |
| 50Li$_2$S·50P$_2$S$_5$ glass | 230                    | 360                   | 3.390                                         | 1.910                                 | 1.89                      | 6.9                    | 18                      | 0.27                   |
| 70Li$_2$S·30P$_2$S$_5$ glass | 25                    | 360                   | 3.330                                         | 1.820                                 | 1.67                      | 5.5                    | 14                      | 0.29                   |
| 70Li$_2$S·30P$_2$S$_5$ glass | 240                    | 360                   | 4.020                                         | 2.090                                 | 1.91                      | 8.3                    | 22                      | 0.31                   |
| 75Li$_2$S·25P$_2$S$_5$ glass | 25                    | 360                   | 2.800                                         | 1.540                                 | 1.45                      | 3.4                    | 8.8                     | 0.28                   |
| 75Li$_2$S·25P$_2$S$_5$ glass | 25                    | 360                   | 3.520                                         | 1.870                                 | 1.68                      | 5.9                    | 15                      | 0.30                   |
| 75Li$_2$S·25P$_2$S$_5$ glass | 100                    | 360                   | 3.880                                         | 2.000                                 | 1.86                      | 7.4                    | 20                      | 0.32                   |
| 75Li$_2$S·25P$_2$S$_5$ glass | 150                    | 360                   | 4.040                                         | 2.060                                 | 1.89                      | 8.0                    | 21                      | 0.32                   |
| 75Li$_2$S·25P$_2$S$_5$ glass | 190                    | 360                   | 4.150                                         | 2.150                                 | 1.88                      | 8.7                    | 23                      | 0.32                   |
| 75Li$_2$S·25P$_2$S$_5$ glass-ceramic | 230                    | 360                   | 4.110                                         | 2.090                                 | 1.88                      | 8.2                    | 22                      | 0.33                   |
| 80Li$_2$S·20P$_2$S$_5$ glass | 25                    | 360                   | 3.710                                         | 2.010                                 | 1.66                      | 6.7                    | 17                      | 0.29                   |
| 80Li$_2$S·20P$_2$S$_5$ glass | 25                    | 540                   | 3.920                                         | 2.130                                 | 1.73                      | 7.9                    | 20                      | 0.29                   |
| 80Li$_2$S·20P$_2$S$_5$ glass | 190                    | 360                   | 4.300                                         | 2.270                                 | 1.85                      | 9.5                    | 25                      | 0.31                   |
| 75Na$_2$S·25P$_2$S$_5$ glass | 25                    | 360                   | 3.280                                         | 1.690                                 | 1.87                      | 5.3                    | 14                      | 0.32                   |
| 75Na$_2$S·25P$_2$S$_5$ glass | 170                    | 360                   | 3.670                                         | 1.820                                 | 2.00                      | 6.6                    | 18                      | 0.34                   |
| Li$_2$La$_2$Zr$_2$O$_{12}$ | —                       | —                     | 5.510                                         | 2.760                                 | 4.52                      | 34.0                   | 92                      | 0.33                   |
| 60KNO$_3$·40Ca(NO$_3$)$_2$ | —                       | —                     | 3.340                                         | 1.510                                 | 2.22                      | 5.0                    | 14                      | 0.37                   |
pellet showed a high Young’s modulus of 92 GPa although it was not fully dense. The 60KNO₃·40Ca(NO₃)₂ glass was prepared by the melt quenching method. The obtained glass was transparent and the density was 2.22 g cm⁻³. The Young’s modulus of 60KNO₃·40Ca(NO₃)₂ was 14 GPa. The values were almost the same in a previous report.²⁰)

The Young’s modulus of a glass can be estimated from the bond dissociation energy per unit volume and the ion packing density.²¹) That is, glasses with large cations and/or anions tend to show low Young’s modulus. Actually, the Young’s modulus of 75Na₂S·25P₂S₅ glass was smaller than that of 75Li₂S·25P₂S₅ glass; the size of Na⁺ ions is larger than Li⁺ ions. The coulomb energy between sulfur and sodium atoms in the 75Na₂S·25P₂S₅ glass was smaller than that between sulfur and lithium atoms in the 75Li₂S·25P₂S₅ glass.

The 60KNO₃·40Ca(NO₃)₂ glass showed similar Young’s modulus to Li₂S·P₂S₅ solid electrolytes. The 60KNO₃·40Ca(NO₃)₂ and Li₂S·P₂S₅ glasses are typical ionic glasses consisting large anions such as NO₃⁻, PS₄³⁻, and P₅S₇⁴⁻. As described above, existence of large anions and/or cations decreases Young’s modulus of glasses.

The reasonability of the Young’s modulus was also confirmed by the compression tests. Stress–strain curve in compression test for the 75Li₂S·25P₂S₅ glass rod is shown in Fig. 2. The glass rod was prepared by hot press; the size was 4 × 4 × 8 mm. The slope was straight below 130 MPa and slightly changes to be gentle above 130 MPa. The Young’s modulus calculated based on the slope below 130 MPa of the stress–strain curve is ca. 17 GPa.

The Young’s modulus calculated from the stress–strain curve is similar to that measured by the ultrasonic sound velocity measurement (23 GPa). The change of the slope indicates that small degree of plastic deformation occurs before fracture. This phenomenon would relate to the high mechanical processability of Li₂S·P₂S₅ solid electrolytes. Further studies should be needed to clarify the details.

Young’s moduli of various materials were shown in Fig. 3. The Young’s moduli of Li₂S·P₂S₅ glasses are lower than those of oxide glasses and most transition metals and higher than polymers.⁶,²²,²³) Sulfides have lower bond dissociation energy per unit volume and lower ion packing density than oxides; sulfide glasses have thus lower Young’s moduli than oxide glasses.

4. Conclusion

The Young’s moduli of Li₂S·P₂S₅ glassy solid electrolytes were measured by ultrasonic sound velocity measurements. The Young’s moduli of the solid electrolytes were about 20 GPa. The Young’s modulus increased with an increase of Li₂S content. The Young’s moduli of Li₂S–P₂S₅ glasses were lower than those of oxide based solid electrolytes. The Young’s moduli of Li₂S–P₂S₅ glasses prepared using various conditions were also measured. The pellets had high packing density even by pressing under glass transition temperature and showed Young’s moduli close to the almost fully dense pellets. The reasonability of the value obtained by the ultrasonic measurement was confirmed by the compression test.

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