1. Introduction

Much attention has been paid to all-solid-state batteries using inorganic solid electrolytes as potential candidates for large-scale energy storage applications such as electric vehicles and smart grids.1-3 Solid electrolytes are key materials for the development of all-solid-state batteries and are preferred for their high ionic conductivity, thermal stability, chemical stability to positive and negative electrode active materials, and mechanical properties, such as softness, that allow them to accommodate volume changes in electrode active materials.4-8 The mechanical properties of solid electrolytes are particularly unique and critical for all-solid-state batteries.

There are two categories of inorganic solid electrolytes: oxides and sulfides. Most of the oxide electrolytes are stiff ceramics, with elastic moduli in the 100–200 GPa range.9 Oxide ceramic electrolytes require sintering at temperatures over 1000°C to reduce the resistance at grain boundaries.9-12 Such high temperatures lead to undesirable side reactions between the electrode/electrolyte interfaces, which cause the cell capacities to decrease. Reducing the sintering temperature13-16 and additional experimental procedures such as screen-printing,17 aerosol deposition,18 or mixing with polymer or gel-polymer electrolytes19-22 are used to improve the interfacial issues in all-solid-state batteries using oxide ceramic electrolytes. On the other hand, all-solid-state batteries using sulfide electrolytes achieve high cell capacities and long cycle performance by simply pressing the powders of solid electrolytes and electrode active materials at room temperature.1,23 We have previously reported favorable mechanical properties of the Li2S–P2S5 glass electrolytes with high lithium-ion conductivities.7,24 Li2S–P2S5 glasses have low Young’s moduli (18–25 GPa) and excellent formability allowing them to be highly densified by pressing even at room temperature.7 These “soft” mechanical properties of the sulfide electrolytes contribute to forming good contacts at the solid-solid interfaces between the solid electrolytes and electrode active materials, leading to excellent electrochemical performances of the cells. Thus, sulfide electrolytes such as the Li2S–P2S5 glass systems have interesting mechanical properties, making them the appropriate choices for all-solid-state batteries. Since sulfide electrolytes are unstable in air, there have not been sufficient studies conducted to evaluate their mechanical properties, therefore further studies are required.
The following three types of sulfide electrolytes have been reported: crystalline, glass, and glass-ceramic materials. Conductivities of glass electrolytes are not extremely high compared to those of crystalline solid electrolytes such as Li10GeP2S12.\(^{25,26}\) Li9.54Si1.74P1.44S11.7Cl0.3,\(^{4}\) and Li1P2S11,\(^{27}\) which exhibit conductivities in the 10\(^{-2}\) S cm\(^{-1}\) order. However, glass electrolytes have several advantages. They have few grain boundaries because of their isotropic structure, which reduces the interfacial resistances in all-solid-state batteries. Decreasing the risk of short-circuiting with the growth of Li dendrites through the grain boundaries is also considered an advantage. In addition, since glass is composed of a former and a modifier, it can present a wide range of compositions. Controlling them leads to the formability of 75Li2S·25P2S5 (mol\%).

Moreover, we assume that the mechanical properties of glasses in the following three systems: 1) Li2S–P2S5 where P2S5 is totally replaced by SiS2 or GeS2 (Li2S–SiS2, Li2S–GeS2, and Li2S–P2S5–GeS2). 2) Li2S–P2S5, where S is totally or partially replaced by O (Li2O–P2S5, Li2S–Li2O–P2S5, and LiSi–P2S5–Li2O), and 3) Li2S–P2S5, where Li2S is totally replaced by Na2S, Ag2S, MgS, and SnS (R2S–P2S5, R = Na, Ag, Mg, Sn). We investigated the effects of changing the glass former and modifier on the mechanical properties of the sulfide glasses. Moreover, we assume that the mechanical properties of the glass and crystalline materials would be different, but the relationship has not been clarified. Thus, we compared the mechanical properties of 75Li2S·25P2S5 (mol\%) glasses, glass-ceramics, and crystals. The elastic moduli of the sulfide glass electrolytes were measured using the ultrasonic pulse echo method and we used their mean atomic volumes\(^{35}\) to summarize the measured elastic moduli. We evaluated the formability using the relative densities and microstructures of the powder-compaction pellets pressed at room temperature and we also discussed the relationship between elastic moduli and formability.

2. Experimental procedure

2.1 Sample preparation

All Li2S–P2S5-based glasses were prepared by implementing a mechanochemical technique using a planetary ball mill. We used reagent-grade Li2S (Idemitsu Kosan or Mitsuwa Chemical, > 99.9%), P2S5 (Aldrich, > 99%), Li2O (Furuuchi Chemical, 99.9%), P2O5 (Kojundo Chemical, 99.99%), GeS2 (Furuuchi Chemical, 99.999%), SiS2 (Furuuchi Chemical, 99.9%), Na2S (Nagao, 99.1%), Ag2S (Aldrich, 99.9%), SnS (Kojundo Chemical, 99.9%), and MgS (Kojundo Chemical, 99.9%) powders as starting materials. These starting materials in stoichiometric proportions were ball-milled until amorphous samples were obtained. 75Li2S·25P2S5 (mol\%: Li1P2S11) glass-ceramic powders were prepared by heating the glass powders at 235°C for 2 h in a dry Ar atmosphere. Moreover, crystalline powders with a 75Li1S·25P2S5 (mol\%) composition were synthesized by carrying out solid phase reactions using Li2S and P2S5.\(^{36}\) A mixture of Li2S and P2S5 powders was placed into a carbon crucible in an Ar-filled glove box and sealed in a quartz tube in vacuum. The quartz tube was heated at 500°C for 5 days and slowly cooled to room temperature.

2.2 Sample characterization

We evaluated the elastic moduli mainly for the hot-pressed pellets using an ultrasonic pulse-echo technique with 5 MHz frequency transducers. The details of the experimental procedures were reported in our previous papers.\(^{7,37,38}\) The hot-pressed pellets were prepared by pelleting the powders at 270 or 360 MPa at near their glass transition temperatures for 4 h in a Ar-filled glove box. The thickness and diameter of the prepared pellets were approximately 2–3 and 10 mm, respectively. The densities of the pellets prepared by hot pressing (\(\rho_{\text{HP}}\)) were measured from the mass and dimensions. We calculated the elastic moduli of the samples using the following equations:

\[
G = \rho_{\text{HP}}V_{S}^{2}
\]

\[
v = (V_{L}^{2} - 2V_{S}^{2})/(V_{L}^{2} - V_{S}^{2})
\]

\[
E = 2G(1 + \nu)
\]

\[
B = E/(3(1 - 2\nu))
\]

where \(V_{S}\) and \(V_{L}\) are the velocities of the shear and longitudinal waves, \(G\) is the shear modulus, \(\nu\) is the Poisson’s ratio, \(E\) is the Young’s modulus, and \(B\) is the bulk modulus.

We investigated the formability from the viewpoint of the relative densities and microstructures of the powder-compressed pellets. The glass powders were cold-pressed mainly at 360 MPa to evaluate the behavior of densification at room temperature. We determined the density of the obtained 10 mm pellets (\(\rho_{\text{bulk}}\)) from their mass and dimensions, and we evaluated the densities of the glass powders (\(\rho_{s}\)) using a gas pycnometer (AccuPyc II 1340, Shimazu) placed in an Ar atmosphere. We calculated the relative densities as \(\rho_{\text{bulk}}/\rho_{s}\) or \(\rho_{\text{bulk}}/\rho_{\text{HP}}\). The microstructures of the pellets were observed using scanning electron microscopy (SEM) measurements using a SEM; JSM-6610A, JEOL or a JE-SEM; SU8200, Hitachi.

3. Results and discussion

3.1 Young’s moduli of the sulfide glasses measured using an ultrasonic pulse-echo technique

We summarized all the elastic moduli of sulfide glasses...
measured here in Table 1. We also listed the already measured ones previously reported in the literature \(^{34,37,38}\) in the same table. Young’s moduli of oxide glasses can be estimated in terms of bond dissociation energy per unit volume of bond dissociation energy, \(\frac{E_B}{V_B}\). We discuss the measured Young’s moduli of sulfide glasses based on these two factors. In this research, we summarized the Young’s moduli of sulfide glasses using mean atomic volumes\(^{35}\) because ion packing densities of the glasses can be easily estimated by calculating the mean atomic volumes from their densities. The powder densities are basically used for calculations, but the densities of the hot-pressed bodies are sometimes used when the powder densities are not measured ones previously reported in the literature\(^{24,37,38}\). The relative density is calculated from the powder density (\(\rho_p\)), shear modulus (\(G\)), Young’s modulus (\(E\)), bulk modulus (\(B\)), and Poisson’s ratio (\(\nu\)) of hot-pressed bodies of sulfide glasses. The glass transition temperature (\(T_g\)) and molding conditions to prepare the hot-pressed bodies are also indicated in the table. The relative density is calculated from the powder density (\(\rho_p\)) of milled glasses.

Table 1. Longitudinal velocity (\(V_L\)), shear velocity (\(V_S\)), hot-press density (\(\rho_{HP}\)), shear modulus (\(G\)), Young’s modulus (\(E\)), bulk modulus (\(B\)), and Poisson’s ratio (\(\nu\)) of hot-pressed bodies of sulfide glasses. The glass transition temperature (\(T_g\)) and molding conditions to prepare the hot-pressed bodies are also indicated in the table. The relative density is calculated from the powder density (\(\rho_p\)) of milled glasses.

| Sample | Powder density (\(\rho_p\))/g·cm\(^{-3}\) | Molding condition | Hot-press density (\(\rho_{HP}\))/g·cm\(^{-3}\) | Relative density (\(\rho_{HP}/\rho_p\))/% | \(V_L\)/m·s\(^{-1}\) | \(V_S\)/m·s\(^{-1}\) | \(G\)/GPa | \(E\)/GPa | \(B\)/GPa | \(\nu\) |
|--------|---------------------------------|------------------|---------------------------------|---------------------------------|----------------|----------------|--------|--------|--------|------|
| Li₂S·75P₂S₅ | 2.02 | — | 1.30 | 4 | 270 | 2.00 | 99.1 | 2960 | 1580 | 5.0 | 13.0 | 0.301 | 10.9 |
| 50Li₂S·50P₂S₅ | 1.95 | 224 | 200 | 4 | 360 | 1.95 | 100 | 4040 | 2070 | 8.4 | 22.1 | 0.314 | 20.7 |
| 67Li₂S·33GeS₂ | 1.88 | 213 | (240) | 4 | 360 | 1.88 | 96.6 | (4020) | 2090 | (8.3) | (21.9) | (0.315) | (19.7) |
| 50Li₂S·50SiS₂ | 1.94 | 304 | 310 | 4 | 360 | 1.84 | 95.1 | 4770 | 2540 | 11.9 | 31.0 | 0.302 | 26.1 |
| 60Li₂S·40GeS₂ | — | 241 | 220 | 4 | 360 | 2.20 | — | 4120 | 2170 | 10.3 | 27.1 | 0.308 | 23.5 |
| 67Li₂S·33GeS₂ | — | 205 | 204 | 4 | 360 | 2.15 | — | 4170 | 2230 | 10.7 | 27.8 | 0.300 | 23.1 |
| 25Li₃P₂S₅·75Li₄GeS₄ | — | 215 | 4 | 360 | 2.13 | — | 4260 | 2230 | 10.6 | 27.7 | 0.311 | 24.5 |
| 50Li₂S·50P₂O₅ | — | 205 | 4 | 360 | 2.06 | — | 4300 | 2200 | 10.0 | 26.3 | 0.323 | 24.8 |
| 75Li₃PS₄·25Li₄GeS₄ | — | 195 | 4 | 360 | 1.98 | — | 4200 | 2140 | 9.1 | 24.0 | 0.325 | 22.8 |
| 50Li₂S·50SiS₂ | (2.07) | 173 | (180) | 4 | 360 | 2.05 | (99.2) | (3280) | (1640) | (5.5) | (14.7) | (0.333) | (14.7) |
| 60Li₂S·40GeS₂ | (2.03) | 194 | (190) | 4 | 360 | 2.01 | (99.0) | (3830) | (1860) | (7.0) | (18.7) | (0.346) | (20.2) |
| 75Li₃PS₄·25Li₄GeS₄ | (2.00) | 170 | (170) | 4 | 360 | 1.98 | (98.9) | (3890) | (1900) | (7.1) | (19.2) | (0.343) | (20.4) |
| 50Ag₂S·50P₂S₅ | 3.40 | 186 | 180 | 4 | 360 | 3.43 | 100.9 | 2620 | 1430 | 7.0 | 18.0 | 0.288 | 14.2 |
| 50Sn₂S·50P₂S₅ | 2.72 | 207 | 190 | 4 | 270 | 2.55 | 93.8 | 2960 | 1550 | 6.1 | 16.1 | 0.311 | 14.2 |
| 67Sn₂S·33P₂S₅ | 3.19 | 217 | 190 | 4 | 270 | 3.01 | 94.3 | 2770 | 1510 | 6.9 | 17.7 | 0.289 | 13.9 |
| 75Sn₂S·25P₂S₅ | 3.47 | 200 | 4 | 270 | 3.46 | 99.7 | 3000 | 1570 | 8.5 | 22.4 | 0.311 | 19.8 |
| 50Mg₂S·50P₂S₅ | 2.08 | 238 | R.T. | 1.5 | 800 | 1.98 | 95.5 | 2650 | 1570 | 4.9 | 12.0 | 0.230 | 7.4 |

Parentheses indicates data from reference \(^{*,34}\), \(^{**,37}\), and \(^{***,38}\).
The dissociation energy is the standard enthalpy change of the simple fission reaction (A-B → A + B) and it is not equivalent to the bonding energy in the glass estimated from Sun’s model.45)

Ion-conducting glasses are composed of the glass former and modifier. The elastic moduli of the Li$_2$S-P$_2$S$_5$ glasses where P$_2$S$_5$ is totally or partially replaced by other glass formers and those where S is partially replaced by O are also shown in Table 1. The relationship between Young’s moduli and the mean atomic volumes is displayed in Fig. 2. Young’s moduli of the Li$_2$S-SiS$_2$ and Li$_2$S-GeS$_2$ glasses are higher than those of the Li$_2$S-P$_2$S$_5$ glasses. On the other hand, the mean atomic volume of the 50Li$_2$S-50SiS$_2$ glass is smaller than that of the 50Li$_2$S-50P$_2$S$_5$ glass. Comparing the ortho-compositions, the 67Li$_2$S-33GeS$_2$ glass has a smaller mean atomic volume than the 75Li$_2$S-25P$_2$S$_5$ glass. In addition, Young’s moduli of the Li$_2$P$_2$S$_5$-Li$_4$GeS$_4$ glasses increase with an increase in the Ge content, while the mean atomic volumes of these glasses decrease with an increase in the Ge content. It seems that Young’s moduli for these glasses have a roughly negative correlation with the mean atomic volumes. Young’s moduli of the oxygen-substituted Li$_2$S-P$_2$S$_5$-P$_2$O$_5$ and Li$_2$O-Li$_2$S-P$_2$S$_5$ glasses also have the same relationships with the mean atomic volumes. Of course, Young’s moduli are also affected by the bond dissociation energies (Li-S: 313 kJ mol$^{-1}$, P-S: 442 kJ mol$^{-1}$, Ge-S: 534 kJ mol$^{-1}$, Si-S: 617 kJ mol$^{-1}$, Li-O: 341 kJ mol$^{-1}$ and P-O: 589 kJ mol$^{-1}$)44) in addition to the mean atomic volumes. The bond dissociation energies of the Ge-S, Si-S, and P-O bonds are larger than that of the P-S bond, corresponding to the increase in Young’s moduli.

Table 1 also shows the elastic moduli of the Li$_2$S-P$_2$S$_5$ glasses where Li$_2$S is fully replaced by other sulfide-modifiers such as: Na$_2$S, Ag$_2$S, Sn$_2$S, and MgS. Their Young’s moduli increase with the increase in each modifier content, while the mean atomic volumes decrease upon the addition of their modifiers (Fig. 3). On the other hand, a negative correlation between Young’s moduli and the mean atomic volume is observed in the meta-composition (denoted as 50-50 in Fig. 3) except for Sn. Since the bonding dissociation energies are reported as Li-S: 313 kJ mol$^{-1}$, Na-S: no data, Ag-S: 217 kJ mol$^{-1}$, Sn-S: 467 kJ mol$^{-1}$, and Mg-S: 234 kJ mol$^{-1}$, the relatively higher bond dissociation energies of the Sn-S bonds might increase Young’s moduli.

Young’s moduli of sulfide glasses studied here are summarized in Fig. 4, along with those of sulfide glasses previously reported in our studies,44,47,38,46 oxide glasses,47-51 and other chalcogenide glasses.53-55 In general, there is a good correlation between Young’s moduli and mean atomic volumes. Oxide glasses (the orange, green, and gray areas) have higher Young’s moduli and smaller mean atomic volumes. Already reported chalcogenide glasses (the purple area) have lower Young’s moduli and larger mean atomic volumes. The sulfide glasses studied here (the blue area) are placed in the intermediate region between the oxide and other chalcogenide glasses.

### 3.2 Formability of sulfide glasses evaluated by powder compaction tests

Table 2 shows the relative density of the Li$_2$S-P$_2$S$_5$ glasses pellets cold-pressed at 360 MPa. The highest relative density is obtained at 75 mol % Li$_2$S content and the lowest at 50 mol %. The more isolated structure at 75 mol % composed of Li$^+$ and P$_2$S$_5^{3-}$ ions may promote better compaction. Rouxel et al. report that a glass with a highly cross-linked network structure (e.g., amorphous silica) has a lower Poisson’s ratio, while a glass with a low-dimensional structure (e.g., bulk metallic glass of...
Zr55Cu30AlNi5) has a higher Poisson’s ratio.\(^{56,57}\) In addition, they suggest that ductility is exhibited in indentation tests with the increase in Poisson’s ratio,\(^{56}\) which means that a glass structure with less connectivity tends to exhibit ductile behavior. This suggestion corresponds to our results that glasses with modifier-rich compositions are more easily densified.

We compared the formability of the 75Li2S·25P2S5 (Li3PS4) glass, glass-ceramic, and crystal. Figure S1 shows the X-ray diffraction (XRD) patterns of the as-prepared crystalline samples. The \(\beta\)-Li3PS4 and \(\gamma\)-Li3PS4 phases are observed for the glass-ceramic and crystal synthesized by solid phase reactions, respectively. For more accurate measurements on formability, we sieved the prepared powders so that the maximum size of the sample should be less than 53 \(\mu\)m. After sieving, the powders have almost the same size as the secondary particles (Fig. S2). Figure 5(a) shows the molding pressure dependence of the relative density of these materials. The relative density of the glass is smaller than those of the glass-ceramics and crystals at lower pressure. At lower pressures, it is assumed that the rearrangement of the particles is dominant for powder-compaction.\(^{58}\) The powder-compaction by rearrangement is affected by the original size of the particles, whose distribution might still remain heterogeneous even after sieving. On the other hand, the relative density of the glass is larger than that of the other two crystalline materials at higher pressures. Cross-sectional SEM images of these materials after cold-pressing at 36, 180, and 360 MPa are shown in Fig. 5(b). Highly densified areas with grains larger than the original ones are observed in the glass compacts at 360 MPa. The voids and grain boundaries in the glass compacts can be easily reduced by only cold-pressing due to the isotropic structure with free volume of the glass. Here, permanent densification, which appeared in germanium sulfide glass by applying the pressure of more than 1.5 GPa,\(^{59}\) has not been considered because of one order of magnitude lower pressure in this study. We assume that free volume in the Li3PS4 glass promotes powder-compaction by plastic flow of atoms/ions, although permanent densification behaviors should be monitored and discussed by applying further pressures in the near future.

The better formability of the glass is important to form solid-solid interfaces between the electrode active materials and solid electrolytes in the bulk-type all-solid-state batteries.\(^7\)

The relative densities of the cold-pressed Li2S–P2S5 glasses where P2S5 is replaced by the other glass formers and those where S is replaced by O are also listed in Table 2.

### Table 2. Relative density of cold-pressed pellets of Li2S–P2S5 glasses where P2S5 is totally or partially replaced by other glass formers, that glasses where S is totally or partially replaced by O, and that glasses where Li2S is replaced by other sulfide-modifiers such as: Na2S, Ag2S, SnS, and MgS. The relative density is calculated from the powder density or hot-press density.

| Composition / mol % | Relative density \((\rho_{\text{bulk}}/\rho_0 \text{ or } \rho_{\text{bulk}}/\rho_{\text{HP}})/\%\) |
|---------------------|----------------------------------|
| 50Li2S·50P2S5       | 85.0                             |
| 67Li2S·33P2S5       | 85.9                             |
| 75Li2S·25P2S5       | 90.4                             |
| 50Li2S·50SiS2       | 75.7                             |
| 50Li2S·50GeS2       | (76)                             |
| 60Li2S·40GeS2       | (81)                             |
| 67Li2S·33GeS2       | (83)                             |
| 25Li2S·75Li4GeS4    | (82)                             |
| 50Li2S·50Li4GeS4    | (83)                             |
| 75Li2S·25Li4GeS4    | (86)                             |
| 70Li2S·20P2S5·10P2O5| (83)                             |
| 50Li2O·50P2O5       | (72.2)                           |

Parentheses indicates the relative density calculated using the density of the hot-pressed pellet.
Table 2. The highest relative density in the Li$_2$S–GeS$_2$ system is obtained at 67 mol% Li$_2$S content (orthocomposition) and the lowest at 50 mol% (meta-composition); a similar trend is observed in the Li$_2$S–P$_2$S$_5$ glasses. On the other hand, the relative densities become smaller by changing the cations of a glass former from P to Ge or Si in the 50Li$_2$S·50M$_x$S$_y$ (M = P, Ge, Si) glasses. Furthermore, the relative densities of the Li$_4$PS$_4$–Li$_4$GeS$_4$ glasses decrease with an increase in the Ge content. As shown in Fig. S3, the SEM images of the fracture cross section of the pellets cold-pressed at 360 MPa reveal that the amounts of voids and grain boundaries increase with an increase in the Ge content. There are two factors to be considered for the difference of formability among glass-forming cations: the glass network connectivity and the mean atomic volume. The number of sulfur for cross-linking is three for P (P is fourfold coordinated to sulfur, but a P–S bond is not involved in the connection in the glass network), and it is four for Ge or Si. In addition, P–S bonds have more covalent character than Ge–S or Si–S bonds. Thus, it is assumed that isolated structures are formed more preferably in the glass containing P as the glass former cation. The isolated structure can facilitate powder-compaction by pressure. In addition, Li$_2$S–P$_2$S$_5$ glasses have larger mean atomic volumes than the Li$_2$S–GeS$_2$ and Li$_2$S–SiS$_2$ glasses, indicating that the Li$_2$S–P$_2$S$_5$ glasses have a larger free volume in the glass structure. The larger free volume will be the other important factor for compaction. On the other hand, replacing S with O in the Li$_2$S–P$_2$S$_5$ glasses decreases the relative density of the glasses, as indicated in Table 2. The formability is obviously different between the 50Li$_2$S·50P$_2$S$_5$ sulfide and

Fig. 5. (a) Molding pressure dependence of the relative density of the 75Li$_2$S·25P$_2$S$_5$ glass, glass-ceramic (g.c.), and crystal. (b) SEM images of the fracture cross sections of these materials after cold-pressing at 36, 180, and 360 MPa respectively.
50Li2O·50P2O5 oxide glasses, as shown in the cross-sectional SEM images of the powder-pressed bodies after cold-pressing at 360 MPa (Fig. S4). It is assumed that oxide glasses have more rigid glass networks because the bonding dissociation energies of the oxide glasses are higher than those of the sulfide glasses (P–S: 442 kJ mol⁻¹, Li–S: 313 kJ mol⁻¹, P–O: 589 kJ mol⁻¹, Li–O: 341 kJ mol⁻¹). In addition, the mean atomic volumes decrease by replacing S with O, as shown in Fig. 2; thus, the rigid structure with a smaller free volume of oxide glasses may disturb the compaction by pressure.

The relative densities of Li2S–P2S5 glasses where Li2S is replaced by other sulfide-modifiers after cold-pressing at 360 MPa are also shown in Table 2. The relative densities increase with an increase in the content of glass modifiers as shown in Fig. 6(a). As for the Li2S–P2S5 glasses, it is considered that increasing the isolated ion structure contributes to an increase in the relative density in the Na2S–P2S5 and SnS–P2S5 systems. Powder-compaction will be prevented if the interaction between the cation of the glass modifier and S is stronger. The strength of the interaction between the cation of the glass modifier and S is estimated using the cation field strength (Z/r²; Z: cation charge, r: cation radius). We plotted the relative densities of the 50R2S·50P2S5 glasses (R = Li, Na, Ag, and Mg) in Fig. 6(b), based on the differences in the cation field strengths. The relative density of the 50SnS·50P2S5 glass is excluded from the graph because the ionic radius of Sn²⁺ is not well defined because of its irregular coordination. The relative densities of the 50R2S·50P2S5 glasses decrease with the increase in the cation field strength except for the 50Ag2S·50P2S5 glass. The Ag–S bond has more covalent character than the other R–S bonds, and that might interfere with the compaction.

Pugh’s ratios (B/G) (B is the bulk and G the shear modulus) are used as ductile-brittle evaluation parameters of the materials and are applied to the solid electrolytes. It is assumed that ductile-brittle properties affect the densification of the glasses in powder-compaction tests. The relationships between B/G and the relative density of the Li2S–P2S5-based glasses in powder-compaction tests are shown in Fig. 7. The glass with a larger B/G ratio, meaning higher ductility, tends to display a higher relative density. The powder-compaction tests were carried out at a high pressure (360 MPa) and room temperature, which is below the glass transition temperatures. The results of Fig. 7 suggest that plastic deformation of the particles mainly contributes to the powder-compaction of these sulfide glasses. It is noted that the lower bonding energy, the larger free volume, and the more isolated structure of sulfide glasses lead to superior mechanical properties.

4. Conclusions

We investigated the mechanical properties of sulfide glasses from the viewpoint of the elastic moduli and formability. Young’s moduli for the Li2S–P2S5 glasses increased with an increase in the Li2S content. The addition of Li2S transformed local structures from chain to isolated structures. It is suggested that the more isolated structures increased the ion packing density and led to an increase of the Young’s moduli. The Young’s moduli of element-substituted Li2S–P2S5 glasses were also evaluated and compared with oxide and other chalcogenide glasses. The Young’s moduli of the Li2S–P2S5 glasses increased
when replacing the glass former of P$_2$S$_5$ with GeS$_2$ or SiS$_2$. The Young’s moduli also increased by substituting S with O. In addition, we investigated the elastic moduli of the Li$_2$S–P$_2$S$_5$ glasses where Li$_2$S was fully replaced by other sulfide-modifiers such as Na$_2$S, Ag$_2$S, SnS, and MgS. The Young’s moduli of these glasses increased with an increase in the content of each modifier. The Young’s moduli studied here were summarized from the viewpoint of the mean atomic volumes. A good correlation between the moduli and mean atomic volumes was found in sulfide glasses as well as oxide and other chalcogenide glasses.

We investigated the formability of these sulfide glasses based on the relative density of the pellets powder-compressed at 360 MPa. The 75Li$_2$S:25P$_2$S$_5$ (mol %) glasses composed of Li$^+$ and PS$_3^{3-}$ ions, which is the most isolated structure in Li$_2$S–P$_2$S$_5$ glasses, exhibited better powder-compaction by pressure. We also evaluated the difference in formability between Li$_2$S–P$_2$S$_5$ glasses, glass-ceramics, and crystals. The glasses showed higher compaction than the crystals because of the isotropic structure with the free volume. The formability of the Li$_2$S–P$_2$S$_5$ glasses is better than that of the Li$_2$S–SiS$_2$ and Li$_2$S–GeS$_2$ glasses. Moreover, it is suggested that the cation field strength of glass modifiers is related to the glass formability. Pugh’s ratio ($B/G$) was used to evaluate the ductile-brittle property of materials. The glasses with a larger $B/G$ ratio, meaning higher ductility, tended to show a higher relative density. We suggested that plastic deformation affected the densification of sulfide glasses in powder compaction tests due to their lower bonding energy, larger free volume, and more isolated structure.

Acknowledgements This research was financially supported by the Japanese Science and Technology Agency (JST), the Advanced Low Carbon Technology Research and Development Program (ALCA), and the Specially Promoted Research for Innovative Next Generation Batteries (SPRING) Project.

References
1) A. Hayashi, A. Sakuda and M. Tatsumisago, *Front. Energy Res.*, 4, 1–13 (2016).
2) J. Janek and W. G. Zeier, *Nat. Energy*, 1, 16141 (2016).
3) A. Manthiram, X. Yu and S. Wang, *Nat. Rev. Mater.*, 2, 16103 (2017).
4) Y. Kato, S. Hori, T. Saito, K. Suzuki, M. Hirayama, A. Mitsu, M. Yonemura, H. Iba and R. Kanno, *Nat. Energy*, 1, 16030 (2016).
5) Y. Wang, W. D. Richards, S. P. Ong, L. J. Miara, J. C. Kim, Y. Mo and G. Ceder, *Nat. Mater.*, 14, 1026–1031 (2015).
6) Y. Zhu, X. He and Y. Mo, *ACS Appl. Mater. Interfaces*, 7, 23685–23693 (2015).
7) A. Sakuda, A. Hayashi and M. Tatsumisago, *Sci. Rep.*, 3, 2261 (2013).
8) A. Sakuda, A. Hayashi and M. Tatsumisago, *Curr. Opin. Electrochem.*, 6, 108–114 (2017).
9) J. Wolfenstine, J. L. Allen, J. Sakamoto, D. J. Siegel and H. Choe, *Ionics*, 24, 1271–1276 (2018).
10) Y. Inaguma, C. Liquan, M. Itoh, T. Nakamura, T. Uchida, H. Ikuta and M. Wakihara, *Solid State Commun.*, 86, 689–693 (1993).
11) M. Huang, T. Liu, Y. Deng, H. Geng, Y. Shen, Y. Lin and C. W. Nan, *Solid State Ionics*, 204–205, 41–45 (2011).
12) Y. Thangadurai and W. Weppner, *J. Solid State Chem.*, 179, 974–984 (2006).
13) K. Tadanaga, R. Takano, T. Ichinose, S. Mori, A. Hayashi and M. Tatsumisago, *Electrochem. Commun.*, 33, 51–54 (2013).
14) R. Takano, K. Tadanaga, A. Hayashi and M. Tatsumisago, *Solid State Ionics*, 255, 104–107 (2014).
15) S. W. Back, J. M. Lee, T. Y. Kim, M. S. Song and Y. Park, *J. Power Sources*, 249, 197–206 (2014).
16) S. Ohta, J. Seki, Y. Yagi, Y. Kihira, T. Tani and T. Asaoka, *J. Power Sources*, 265, 40–44 (2014).
17) S. Ohta, S. Komagata, J. Seki, T. Saeki, S. Morishita and T. Asaoka, *J. Power Sources*, 238, 53–56 (2013).
18) T. Kato, S. Iwasaki, Y. Ishii, M. Motoyama, W. C. West, Y. Yamamoto and Y. Iriyama, *J. Power Sources*, 303, 65–72 (2016).
19) W. Zhou, S. Wang, Y. Li, S. Xin, A. Manthiram and J. B. Goodenough, *J. Am. Chem. Soc.*, 138, 9385–9388 (2016).
20) X. Tao, Y. Liu, W. Liu, G. Zhou, J. Zhao, D. Lin, C. Zu, O. Sheng, W. Zhang, H. W. Lee and Y. Cui, *Nano Lett.*, 17, 2967–2972 (2017).
21) J. Zhang, X. Zang, H. Wen, T. Dong, J. Chai, Y. Li, B. Chen, J. Zhao, S. Dong, J. Ma, L. Yue, Z. Liu, X. Guo, G. Cui and L. Chen, *J. Mater. Chem. A*, 5, 4940–4948 (2017).
22) K. Yoshima, Y. Harada and N. Takami, *J. Power Sources*, 302, 283–290 (2016).
23) M. Tatsumisago and A. Hayashi, *Int. J. Appl. Glass Sci.*, 5, 226–235 (2014).
24) A. Sakuda, A. Hayashi, Y. Takigawa, K. Higashi and M. Tatsumisago, *J. Ceram. Soc. Jpn.*, 121, 946–949 (2013).
25) N. Kamaya, K. Homma, Y. Yamakawa, M. Hirayama, R. Kanno, M. Yonemura, T. Kamiyama, Y. Kato, S. Ham, K. Kawamoto and A. Mitsui, *Nat. Mater.*, 10, 682–686 (2011).
26) Y. Sun, K. Suzuki, S. Hori, M. Hirayama and R. Kanno, *Chem. Mater.*, 29, 5858–5864 (2017).
27) Y. Seino, T. Ota, K. Takada, A. Hayashi and M. Tatsumisago, *Energy Environ. Sci.*, 7, 627–631 (2014).
28) K. Minami, A. Hayashi, S. Ujiie and M. Tatsumisago, *Solid State Ionics*, 192, 122–125 (2011).
29) T. Ohtomo, F. Mizuno, A. Hayashi, K. Tadanaga and M. Tatsumisago, *J. Power Sources*, 146, 715–718 (2005).
30) T. Ohtomo, A. Hayashi, M. Tatsumisago and K. Kawamoto, *J. Non-Cryst. Solids*, 364, 57–61 (2013).
31) M. Ménétrier, C. Estournès, A. Levasseur and K. J. Rao, *Solid State Ionics*, 53–56, 1208–1213 (1992).
32) R. Mercier, J. P. Malugani, B. Fahys and G. Robert, *Solid State Ionics*, 5, 663–666 (1981).
33) S. Ujiie, A. Hayashi and M. Tatsumisago, *Mater. Renew. Sustain. Energy*, 3, 1–8 (2014).
34) S. Ujiie, T. Inagaki, A. Hayashi and M. Tatsumisago, *Solid State Ionics*, 253, 57–61 (2014).
35) N. Soga, H. Yamanaka, C. Hisamoto and M. Kunugi, *J. Non-Cryst. Solids*, 22, 67–76 (1976).
36) K. Homma, M. Yonemura, T. Kobayashi, M. Nagao, M. Hirayama and R. Kanno, *Solid State Ionics*, 182, 53–58 (2011).
37) A. Kato, M. Nagao, A. Sakuda, A. Hayashi and M. Tatsumisago, *J. Ceram. Soc. Jpn.*, 122, 552–555 (2014).
38) M. Nose, A. Kato, A. Sakuda, A. Hayashi and M. Tatsumisago, *J. Mater. Chem. A*, 3, 22061–22065 (2015).
39) A. Makishima and J. D. Mackenzie, *J. Non-Cryst. Solids*, 12, 35–45 (1973).
40) S. Inaba, S. Fujino and K. Morinaga, *J. Am. Ceram. Soc.*, 82, 3501–3507 (1999).
41) C. Bischoff, K. Schuller, M. Haynes and S. W. Martin, *J. Non-Cryst. Solids*, 358, 3216–3222 (2012).
42) S. S. Berbano, I. Seo, C. M. Bischoff, K. E. Schuller and S. W. Martin, *J. Non-Cryst. Solids*, 358, 93–98 (2012).
43) K. Ohara, A. Mitsui, M. Mori, Y. Onodera, S. Shiotani, Y. Koyama, Y. Orikasa, M. Murakami, K. Shimoda, K. Mori, T. Fukunaga, H. Arai, Y. Uchimoto and Z. Ogumi, *Sci. Rep.*, 6, 21302 (2016).
44) Y. R. Luo and J. A. Kerr, “CRC handbook of chemistry and physics”, Ed. by D. R. Lide and CRC Press Taylor&amp;Francis, Boca Raton (2006) pp. 9-54–9-59.
45) K. H. Sun, *J. Am. Ceram. Soc.*, 30, 277–281 (1947).
46) A. Kato, M. Yamamoto, A. Sakuda, A. Hayashi and M. Tatsumisago, *ACS Appl. Energy Mater.*, 1, 1002–1007 (2018).
47) K. Takahashi and A. Osaka, *J. Ceram. Soc. Jpn.*, 91, 116–120 (1983).
48) M. Ashizuka, T. Sakai and A. Iwata, *J. Ceram. Soc. Jpn.*, 91, 86–94 (1983).
49) M. Ashizuka and T. Sakai, *J. Ceram. Soc. Jpn.*, 91, 176–182 (1983).