Unique thermal conductivity, Young’s modulus and local structure of 72SnO–28P2O5 glass

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1. Introduction

Tin-phosphate (SnO–P2O5) glasses with high SnO contents have a high potential for new lead-free low-melting sealing frits and optical materials, and it is known that binary SnO–P2O5 glasses containing a large amount of SnO, i.e., up to around 75 mol%, are prepared by conventional melt-quenching method. As one of the prominent optical features, SnO–P2O5 glasses (SnO content: >55 mol %) exhibit large negative- and/or zero stress-optical coefficients. Recently, SnO–P2O5 glasses have been expected as anode active materials for rechargeable lithium ion batteries (LIBs). Yamauchi et al. have demonstrated that a tin-phosphate glass with the composition of 72SnO.28P2O5 is a promising candidate of new anode materials realizing LIBs in which a large number of Q1 ((PO3.52) and Q0 (PO4)3− units are formed. These structural features would be one of the main reasons for the fast diffusion of Li+ ions and result in the excellent LIB performance as anode materials of the glass.

2. Experimental

Glasses with the composition of 72SnO.28P2O5 were prepared by melting a batch of raw materials consisting of SnO, Sn2P2O7, and H3PO4 (aq.) at 950°C in a nitrogen atmosphere using a platinum crucible. The melts were poured onto a carbon plate and annealed from 300°C to room temperature using a furnace. The glass transition (Tg), and crystallization peak (Tc) temperatures of 72SnO.28P2O5 glass powders were determined by using differential thermal analysis (DTA) (Rigaku Thermo Plus TG8120) at a heating rate of 10 K/min in air. Glass powders (∼2 g) with an average diameter of 2 μm were heat-treated at 430°C for 3 h in 5%H2/Ar atmosphere in an alumina boat. The crystalline phases present in the heat-treated samples were identified by using X-ray diffraction (XRD) analysis (Cu Kα radiation) (Rigaku Ultima IV) at room temperature.

The density (ρ) of the glass was determined using the Archimedes method with kerosene as an immersion liquid. The specific heat (Cp) of the glass was measured by using differential scanning calorimetry (DSC) (PerkinElmer: DSC7) in a dry N2 gas flow. The heating rate in DSC measurements was 10 K/min, and standard specimens of alumina (sapphire) were used as a heat capacity standard. The thermal diffusivity (D) of the glass was measured using a flash method (NETZSC. LFA447), in which Xenon lamp and InSb infra-red sensor were used. The sample size was 10 × 10 × 1 mm and carbon was coated on one-side of the plate-shaped sample. The Young’s modulus (E) of the glass was measured using a resonance method (Nihon Techno-Plus: JE-RT3). The measurements of ρ, Cp, D, and E at room temperature for the glass prepared in this study were carried out in
the Toray Research Center In. (Otsu, Japan).

Raman scattering spectra at room temperature for the glass and crystallized samples were measured with a laser microspectrometer (REINSHAW: inViaReflex Raman High Speed Mapping System) operated at a laser with a wavelength of λ = 532 nm. The Mössbauer effect measurements were conducted on powder samples spread on a paper at room temperature with a multi-channel analyzer (MCS mode, 512 channel) (Toray Research Center, Inc., Otsu, Japan). A radioactive 119Sn in CaSnO3 matrix was used as the γ-ray source (0.555 GBq), and the velocity calibration was obtained from the 2-line spectra of SnO2. Mössbauer spectra obtained were analyzed (fitted) by using the Lorentz’s functions for singlet and doublet peaks.

3. Results
3.1 Thermal and elastic properties of 72SnO.28P2O5 glass

As reported in the previous papers,[12–14] 72SnO.28P2O5 glass (designated here as 72SnPO glass) prepared has the values of low glass transition and crystallization peak temperatures, i.e., Tg = 247, Tg3 = 334, and Tg2 = 429°C, and the valence state of Sn ions is mainly Sn⁴⁺. The values of density ρ = 4.02 × 10³ kg/m³ (i.e., 4.02 g/cm³), heat capacity Cp = 449 J/kgK, thermal diffusivity D = 0.195 × 10⁻⁶ m²/s, and Young’s modulus E = 30 GPa were obtained for the 72SnPO glass, and these values are summarized in Table 1. The value of the thermal conductivity (κ) for the 72SnPO glass was estimated using the following equation, and the value obtained, i.e., κ = 0.35 W/mK, is shown in Table 1.

\[
κ = \rho \cdot D \cdot C_p
\]

As a feature of the 72SnPO glass, it should be pointed out that the values of the thermal diffusivity and also thermal conductivity are very small compared with other oxide glasses.

For example, as reported by Inaba et al.[15] many SiO2-based glasses show the values of D = 0.36–0.74 × 10⁻⁶ m²/s and κ = 0.6–1.55 W/mK, many B2O3-based glasses have the values D = 0.32–0.50 × 10⁻⁶ m²/s and κ = 0.62–1.09 W/mK, many P2O5-based glasses (e.g., 50Li2O–50P2O5, 50BaO–50P2O5, and 30Na2O–10Al2O3–60P2O5 glasses) provide the values of D = 0.31–0.52 × 10⁻⁶ m²/s and κ = 0.54–0.87 W/mK, and many TeO2 glasses show the values of D = 0.31–0.40 × 10⁻⁶ m²/s and κ = 0.70–0.81 W/mK. These results suggest strongly that the glass with the composition of 72SnO.28P2O5 has a unique glass structure. Furthermore, it should be emphasized that the 72SnPO glass has a very small Young’s modulus of E = 30 GPa, which indicates that the structure of the 72SnPO glass is deformed easily under small applied stresses. This value of E = 30 GPa is much smaller when compared with other SiO2-, B2O3-, P2O5-, and GeO2-based glasses.[15]

Even in comparison with TeO2-based glasses which are typical glasses showing a fragile character, the value of E = 30 GPa observed in the 72SnPO glass is small.[15] For instance, the following values have been reported; E = 44.3 GPa for 20Li2O–80TeO2 glass,[16] E = 54.7 GPa for 15K2O.15Nb2O5.70TeO2 glass which exhibits a bulk nano-crystallization,[16] E = 64.1 GPa for In50O.25Nb2O5.50GeO2 glass which exhibits a bulk nano-crystallization,[16] and E = 34.3 GPa for 45CuO.55P2O5 glass which has unique oxygen coordination and bonding states of Cu⁺ ions.[18] The density of the 72SnPO glass, i.e., ρ = 4.02 × 10³ kg/m³ (i.e., 4.02 g/cm³), is large, because a large amount (72 mol %) of SnO is included in the 72SnPO glass. This value is the almost same as the value of ρ = 4.05 g/cm³ for 72SnO.28P₂O₅ glass reported by Cha et al.[8]

3.2 Raman scattering spectrum of 72SnO.28P2O5 glass

Figures 1 and 2 show the Raman scattering spectra at room temperature for the 72SnPO glass. The 72SnPO glass shows some broad peaks at ~30, ~270, ~440, ~530, ~620, ~740, ~970, and ~1050 cm⁻¹. The Raman scattering spectra for SnO–P₂O₅ glasses have been reported by some researchers so far.[8,9,11] As proposed by Hayashi et al.,[11] the band at ~740 cm⁻¹ is assigned to the P–O–P symmetric stretching vibration in P–O–P network chains, the band at ~970 cm⁻¹ is due to the P–O stretching vibration in orthophosphate (PO₄³⁻, Q⁴), and the band at ~1050 cm⁻¹ is assigned to the P–O stretching vibration in pyrophosphate (PO₃²⁻, Q³), where n in Qⁿ represents the number of bridging oxygen per phosphate tetrahedron. From the composition dependence of Raman scattering spectra, it has been well analyzed that the number of bridging oxygen in the PO₄ tetrahedron in SnO–P₂O₅ glasses decreases with increasing SnO content, i.e., the increase in Q¹ and Q⁰.[9,11] Bekaert et al.[9] examined the structure of SnO(100 – ν)PO₅ glasses (0.30 ≤ ν ≤ 0.75) prepared under argon atmosphere on the ground of ³¹P and ¹¹⁹Sn NMR spectra and reported that Sn⁺ local environment in the glasses is close to a trigonal SnO₂ pyramid. They found that Sn ions are bonded to less and less polymerized Qⁿ sites (Q² down to Q⁰) with a high amount of SnO. As shown in Fig. 2, the relative intensity of the peaks at ~970 and 1050 cm⁻¹ against the peaks at ~30, ~270, ~440, ~530, ~620, ~740, ~970, and ~1050 cm⁻¹ is large, because a large amount (72 mol %) of SnO is included in the 72SnPO glass. This value is the almost same as the value of ρ = 4.05 g/cm³ for 72SnO.28P₂O₅ glass reported by Cha et al.[8]
peak at ~740 cm$^{-1}$ is extremely large, which strongly suggests that even in 72SnPO glass prepared in this study, a large amount of Q$^4$ and Q$^6$ are formed. Sn$^{2+}$ ion possesses an electron lone pair that affects the coordination environment of SnO$_4$ polyhedra. Brow et al.$^{2}$ and Holland et al.$^{3}$ have proposed that the lone pair of Sn$^{2+}$ ion forms the apex of trigonal SnO$_3$ pyramid in phosphate glasses. Such trigonal SnO$_3$ pyramids with lone pairs might induce the lack of strong bonding cross-links, consequently resulting in the relatively low glass transition temperatures in SnO$_x$-P$_2$O$_5$ glasses.$^{30}$ The possibility of the formation of trigonal SnO$_3$ pyramids with lone pairs in 72SnPO glass is very resemble to the formation of trigonal TeO$_3$ pyramids with lone pairs in TeO$_2$-based glasses with a large amount of TeO$_2$.$^{19}$ It is known that TeO$_2$-based glasses have the relatively low glass transition temperature and the so-called fragile character.$^{20,22}$

The bands appeared in the wavenumber region being less than 700 cm$^{-1}$, e.g., ~30 ~270, ~530, and ~620 cm$^{-1}$, have not been assigned well at this moment. The molar mass (Sn: 118.69 g/mol) of tin element is much larger than that (P: 30.97 g/mol) of phosphorus element, and the glass transition temperature of 72SnO.(100 - x)P$_2$O$_5$ glasses tends to decrease with increasing SnO content,$^{30}$ meaning that the force constant of Sn-O bonds is much smaller than that of P-O bonds. Indeed, as reported by Cha et al.$^{8}$ and Lim et al.$^{9}$ the intensity of the bands at the low frequency side in xSnO.(100 - x)P$_2$O$_5$ glasses increases with increasing SnO content. It would be, therefore, reasonable to assign that the low frequency bands shown in Figs. 1 and 2 for 72SnPO glass are closely related to the vibration and bending modes in some structural units consisting of Sn ions.

As seen in Fig. 1, a broad Raman peak with a strong intensity is observed at the extremely low frequency side of ~30 cm$^{-1}$ in 72SnPO glass. That is, 72SnPO glass provides a clearly Boson peak. There has been no discussion about Boson peaks in Raman scattering spectra for SnO$_x$-P$_2$O$_5$ glasses so far. As a general principle, it has been proposed that Boson peaks are connected with some correlation radius of glass structure in the scale of ~1 nm.$^{23}$ The presence of Boson peaks in Raman scattering spectra is, therefore, regarded as one of the experimental evidences for the presence of nano-scale heterogeneous structure in a given glass.

Recently, Takahashi and Fujitaka et al.$^{26}$ performed in situ observations of Boson peaks in crystallizing glasses while elevating temperature in 15K$_2$O-15Nb$_2$O$_5$-70TeO$_2$ (denoted as KNT) and 25K$_2$O-25Nb$_2$O$_5$-50GeO$_2$ (KNG) glasses and found that a drastic decrease in elasticity and damping of Boson peaks takes place during the crystallization process at around the glass transition temperature. They proposed that denser regions in the heterogeneous structure of the glasses transform into crystal nuclei. It should be pointed out that KNT and KNG glasses exhibit prominent homogeneous nucleation i.e., bulk nanocrystallizations, forming nanocrystals and resulting in excellent optical transparencies.$^{25,26}$ Considering the interpretation of Boson peak discussed so far,$^{23,24}$ it would be reasonable to conclude that 72SnO.28P$_2$O$_5$ glass might have a unique glass structure providing a unique nano-scale heterogeneous structure. Nowadays, in oxide glasses, it has been recognized that in a nanometer-scale (i.e., nano-scale) level, glasses are not homogeneous, i.e., the presence of nano-scale heterogeneous structure.$^{27}$ The local structure of 72SnO.28P$_2$O$_5$ glass will be discussed more in the next sections.

### 3.3 Mössbauer spectrum of 72SnO.28P$_2$O$_5$ glass

Figure 3 shows the Mössbauer spectrum at room temperature for the 72SnPO glass, in which the best fitting curves are indicated. It is seen that the Mössbauer spectrum consists of the overlapping of one single and two doublet peaks. In this analysis, because the peaks appeared in the velocities of around +3 mm/s is asymmetric, two kinds of doublet peaks were used. The estimated Mössbauer parameters of isomer shift $\delta$, quadrupole splitting $\Delta$, half width of peak $\Gamma$, and absorption area intensity ratio $S$ are summarized in Table 2. It is seen that Sn ions denoted as the site-I with a single peak have a small isomer shift ($\delta = 0.14$ mm/s) and Sn ions denoted as the site-II and site-III with doublet peaks have large isomer shifts ($\delta = +3.15$ and +3.54 mm/s).

The Mössbauer effect of $^{119}$Sn has been applied to clarify the bonding state and site environment of Sn ions in glassy and crystalline materials so far.$^{7,19,25}$ It is known that Sn$^{4+}$ ions with a formal electronic configuration of [Kr]4d$^{10}$ show small isomer shifts due to the small contribution of s-electrons to the nucleus, e.g., $\delta = +0.004$ mm/s in SnO$_2$ crystals.$^{29}$ On the other hand, Sn$^{2+}$ ions with a formal electronic configuration of [Kr]4d$^{10}$5s$^2$ have large isomer shifts due to the large contribution of s-electrons to the nucleus, e.g., $\delta = +2.871$ mm/s in SnO crys-
Table 2. Mössbauer parameters obtained by fittings for the precursor glass and crystallized samples of 78SnO.28P2O5 (mol%). δ, Δ, Γ, and S are isomer shift, quadrupole splitting, half width of peak, and absorption intensity ratio between Sn2+ and Sn4+ peaks, respectively.

| Sample    | Site     | δ (mm/s) | Δ (mm/s) | Γ (mm/s) | S (%) |
|-----------|----------|----------|----------|----------|-------|
| Glass     | Site-I   | −0.14    | 0        | 1.82     | 4     |
|           | Site-II  | +3.15    | 1.77     | 1.18     | 68    |
|           | Site-III | +3.54    | 1.31     | 1.59     | 28    |
| Crystallized | Site-I   | −0.45    | 0        | 0.99     | 3     |
|           | Site-II  | +2.98    | 1.85     | 0.95     | 48    |
|           | Site-III | +3.51    | 1.46     | 0.94     | 49    |

The Mössbauer spectrum shown in Fig. 3, therefore, a single peak with a small value of δ = −0.14 mm/s for the site-I is assigned to Sn4+ ions, and two doublet peaks with large values of δ = +3.15 mm/s for the site-II and δ = +3.54 mm/s for the site-III are assigned to Sn2+ ions. Ehrt measured the $^{119}$Sn-Mössbauer spectra of 60Sn0.40P2O5 glass and analyzed the asymmetrical spectra using the two-site model for Sn2+ ions. Consequently, they obtained the values of δ = +3.1 mm/s and δ = +3.5 mm/s, being very close to the values obtained in this study. Nishida et al. measured the $^{119}$Sn-Mössbauer spectra of xSnO,(70−x)SnF2.30P2O5 glasses (0 ≤ x ≤ 70) at 78 K and reported that for 70Sn0.30P2O5 glass, a single peak with δ = −0.23 mm/s is assigned to Sn4+ ions and a doublet peak with δ = +3.30 mm/s is assigned to Sn2+ ions. It should be pointed out that the average value of the isomer shifts for the site-II and site-III shown in Table 2, i.e., δ = +3.34 mm/s, is very close to the value of δ = +3.30 mm/s reported by Nishida et al. The presence of two sites with large quadrupole splitting values of Λ = 1.77 and 1.31 mm/s (Table 2), i.e., the site-II and site-III, indicates that Sn2+ ions in 72SnPO glass prepared in this study have mainly two different coordination states with large site distortions (electric field gradients). As seen in Fig. 3 and Table 2, the intensity ratio of the site-I against the site-II and site-III is very small, i.e., 4%, indicating that Sn ions in 72SnPO glass are mainly Sn2+ and the fraction of Sn4+ is extremely small.

### 3.4 Crystallization behavior of 72SnO.28P2O5 glass

Because crystallization of glasses starts from the nano-scale dimension, crystallization behavior, in particular the initial stage of the nucleation and crystal growth, would be affected largely by the nano-scale heterogeneous structure of glasses. In this sense, information on the crystallization behavior of glasses is important for a deep understanding of the structure of glasses. Figure 4 shows the XRD patterns for the samples obtained by heat treatments at 430°C for 3 h in the different atmospheres of 3%H2/Ar and air. The XRD peaks were assigned to two crystalline phases at 430°C for 3 h in the different atmospheres of 3%H2/Ar and air. The XRD peaks were assigned to two crystalline phases at 430°C for 3 h in the different atmospheres of 3%H2/Ar and air. The XRD peaks were assigned to two crystalline phases at 430°C for 3 h in the different atmospheres of 3%H2/Ar and air.

![XRD patterns for the samples obtained by heat treatments at 430°C for 3 h in the different atmospheres of 3%H2/Ar and air for 72SnO.28P2O5.](image)

The Raman scattering spectra at room temperature for the crystallized (430°C, 3 h) sample are shown in Figs. 1 and 2. Many sharp peaks being typical for crystalline materials are observed. It should be pointed out that the band positions in the crystallized sample are almost the same as those in the glass sample. Furthermore, it is noted that the relative intensity of the peak at ~740 cm$^{-1}$ in the crystallized sample is becoming very small, suggesting that the amount of the chain structure consisting of P–O–P bonds present in the glass decreases during the crystallization. As clarified from XRD patterns (Fig. 4), the crystallized sample contains Sn3(PO4)2 crystals with no chain structure of the nearest oxygen atom, and 4) Sn2+ ions occupy three different sites, i.e., Sn(1), Sn(2), and Sn(3), the primary coordination state around Sn(2) is quite similar to that of Sn(1), but the coordination state around Sn(3) is different from those of other two Sn(1) and Sn(2). The overall molecular packing in Sn3(PO4)2 crystal is illustrated in Fig. 5. The β-Sn3P2O7 crystalline phase has the triclinic space group P1 with the lattice parameters of a = 0.52776 nm, b = 1.15413 nm, c = 1.16360 nm, α = 102.911°, β = 99.303°, and γ = 98.899°, and contains the [P$_6$O$_7$]$^{4+}$ pyrophosphate groups oriented in mutually perpendicular directions with Sn2+ situated in large structural interstices.

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P–O–P bonds and \(\beta\)-Sn\(_2\)P\(_2\)O\(_7\) crystals with [P\(_2\)O\(_7\)]\(^{3-}\) units (i.e., P–O–P bonds). It is, therefore, considered that the band at \(\sim 740\) cm\(^{-1}\) observed for the crystallized sample should be assigned to P–O–P bonds in \(\beta\)-Sn\(_2\)P\(_2\)O\(_7\) crystals formed in the residual glassy phase.

Figure 6 shows the Mössbauer spectrum at room temperature for the crystallized (430°C, 3 h) sample, in which the best fitting curves are indicated. As similar to the base glass (Fig. 3), the Mössbauer spectrum is well fitted using the components of one single (site-I) and two doublets peaks (site-II and site III). The estimated Mössbauer parameters are summarized in Table 2. The site-I with a small isomer shift of \(\delta = -0.45\) mm/s and a small peak intensity of \(S = 3\)% would be assigned to Sn\(^{4+}\) ions. The two doublet peaks with large values of \(\delta = +2.98\) mm/s for the site-II and \(\delta = +3.51\) mm/s for the site-III are assigned to Sn\(^{3+}\) ions. It is noted that the peak intensity (\(S = 49\)% of the site III is almost the same as that (\(S = 49\)% of the site III. Chernaya et al.\(^{31}\) reported the Mössbauer parameters of the isomer shift of \(\delta = +3.37\) mm/s and the quadrupole splitting of \(\Delta = 1.47\) mm/s for Sn\(_2\)P\(_2\)O\(_7\) crystals. These values are very close to the values of \(\delta = +3.51\) mm/s and \(\Delta = 1.46\) mm/s for Sn\(_2\)P\(_2\)O\(_7\) crystal. Lee and Flinn\(^{39}\) reported that the isomer shift of Sn\(^{3+}\) in Sn\(_2\)(PO\(_4\))\(_2\) crystal is small when compared with that in \(\beta\)-Sn\(_2\)P\(_2\)O\(_7\) crystal. Because the crystallized sample contains two different crystalline phases of Sn\(_3\)(PO\(_4\))\(_2\) and \(\beta\)-Sn\(_2\)P\(_2\)O\(_7\), it would be reasonable to assign that the site-II and site-III observed for the crystallized sample (Fig. 6) are assigned to Sn\(_3\)(PO\(_4\))\(_2\) and \(\beta\)-Sn\(_2\)P\(_2\)O\(_7\) crystals, respectively. As evaluated from XRD pattern (Fig. 4), the amounts of Sn\(_3\)(PO\(_4\))\(_2\) and Sn\(_2\)P\(_2\)O\(_7\) formed and in the residual glassy phase. Therefore, the peak intensity observed in the Mössbauer spectrum, i.e., 48/49 = 0.98 (Table 2). Therefore, the peak intensity observed in the Mössbauer spectrum also supports that the site-II and site-III observed for the crystallized sample (Fig. 6) are assigned to Sn\(_3\)(PO\(_4\))\(_2\) and \(\beta\)-Sn\(_2\)P\(_2\)O\(_7\) crystals, respectively.

It is noted that the Mössbauer parameters of \(\delta = +3.15\) mm/s and \(\Delta = 1.77\) mm/s for the site-II assigned in the 72SnPO glass, which has a large peak intensity of \(S = 68\)% are close to the average values of \(\delta = +3.24\) mm/s and \(\Delta = 1.65\) mm/s for the site-II [i.e., Sn\(_3\)(PO\(_4\))\(_2\)] and site-III (\(\beta\)-Sn\(_2\)P\(_2\)O\(_7\)) assigned in the crystallized sample. It is, therefore, considered that the coordination polyhedra of Sn\(^{3+}\) ions in 72SnO.28P\(_2\)O\(_5\) glass might be close to the intermediate state between Sn\(_3\)(PO\(_4\))\(_2\) and \(\beta\)-Sn\(_2\)P\(_2\)O\(_7\) crystals. Bekaeft et al.\(^{32}\) proposed that Sn\(^{3+}\) environment in SnO–P\(_2\)O\(_5\) glasses with a high amount of SnO should be close to that in crystalline Sn\(_3\)(PO\(_4\))\(_2\).

4. Discussion

As clarified in the above, 72SnO.28P\(_2\)O\(_5\) glass has the following unique properties and local structures: 1) low glass transition and crystallization temperatures, 2) small thermal diffusivity and thermal conductivity, 3) small Young’s modulus, 4) intense Boson peak, and 5) unique nano-scale heterogeneous structure. In oxide glasses, the thermal conductivity is governed by lattice vibration, i.e., phonon scattering. In order to emphasize a small diffusivity of 72SnPO glass, the relationship between the mean atomic mass and thermal diffusivity in various glasses is shown in Fig. 7. The data besides 72SnPO glass are presented by Fujino and Inaba.\(^{35}\) Again, it is confirmed that 72SnPO glass containing a large amount of SnO (i.e., a large mean atomic mass) has an extremely small thermal diffusivity.
20Na2O.80SiO2 glass has the value of \( l = 0.45 \) nm, 50BaO.50P2O5 glass shows the value of \( l = 0.38 \) nm, and 20Li2O–80TeO2 glass has the value of \( l = 0.50 \) nm. It is, therefore, recognized that the phonon mean free pass of \( l = 0.30 \) nm in 72SnO.28P2O5 glass is very small compared with other oxide glasses. As clarified from the Raman scattering spectra shown in Figs. 1 and 2, a large amount of \( Q^1 \) and \( Q^2 \) units are formed in 72SnPO glass, and thus the continuous (i.e., long distance) network structure consisting of \( P-O-P \) bonds is not expected. This would be one of the main reasons for the small phonon mean free pass estimated in 72SnPO glass. Some studies have been carried out to find a relationship between thermal conductivity and glass structure.36,37 For example, Ghoneim and Halawa36) found that the thermal conductivity of Na2O–B2O3–SiO2 glasses is becoming high with increase in both B2O3 and SiO2, indicating that the formation of a network structure consisting of BO4 and SiO4 tetrahedral units results in a longer phonon mean free path and consequently in a higher thermal conductivity. It would be reasonable to propose that in a given glass system basically glasses consisting of short network structure length have low thermal conductivities, and 72SnO.28P2O5 glass would correspond to this type of glasses.

The packing density provides useful information on the structure of glasses, and it’s value changes depending on the glass composition and coordination number of constituent ions (e.g., \( \text{B}^{3+}, \text{Ge}^{4+}, \text{and Al}^{3+} \) ions).31,32,33) The value of the packing density of 72SnPO glass was calculated using the following equation,1,34,40

\[
V_p = \frac{\Sigma (V_i x_i)}{(M / \rho)}
\]

where \( V_i \) is the packing factor defined for an oxide \( M_iO_{x_i} \), e.g., \( V_i = 8.9 \times 10^{-6} \text{m}^3/\text{mol} \) for SnO and \( V_i = 34.8 \times 10^{-6} \text{m}^3/\text{mol} \) for \( \text{P}_2\text{O}_5 \), \( x_i \) is the molar fraction of the \( i \)th component, and \( M_i \) is the mean molecular weight of the glass, e.g., 136.7208 \( \times \) \( 10^{-3} \) kg/mol for 72SnPO glass. 72SnPO glass with \( \rho = 4.02 \times 10^3 \) kg/m³ is \( V_p = 0.475 \). As reported by Hoppe,38) \( \text{r} \times \text{R} \text{O}(1 - x)\text{P}_2\text{O}_5 \) glasses (\( \text{R} = \text{Zn}, \text{Mg}, \text{Ca}, \text{and Ba} \)) with \( x = 0.05-0.6 \) show the values of \( V_p = 0.50-0.55 \), although ZnO–P2O5 glasses have the values of \( V_p = 0.48-0.54 \). Takahashi et al.41) reported the values of \( V_p \leq 0.51 \) for many CaO–Al2O3–SiO2 glasses, e.g., \( V_p = 0.523 \) for 43CaO.24Al2O3.33SiO2 glass with a low content of the glass-forming oxide SiO2. From the viewpoint of packing density, it is, therefore, considered that the structure of 72SnPO glass might be largely open. It is noted that the packing density of Sn(PO2)2 crystal (i.e., 75SnO.25P2O5) with the density of \( \rho = 4.138 \times 10^3 \text{kg/m}^3 \) is \( V_p = 0.466 \).33) On the other hand, for Sn2P2O6 crystal (67SnO.33P2O5) with the density of \( \rho = 4.088 \times 10^3 \text{kg/m}^3 \) the value of \( V_p = 0.522 \) was estimated. The packing density \( V_p = 0.475 \) of 72SnO.28P2O5 glass is, therefore, very close to that (\( V_p = 0.465 \)) of Sn(PO2)2 crystal which is one of the crystalline phases formed in the crystallization of 72SnO.28P2O5 glass.

From the above discussion, it is expected that 72SnPO glass has an open network structure. Furthermore, because of the low glass transition temperature \( T_g = 247^\circ \text{C} \), an average bond strength in 72SnPO glass would be small. It is considered that these structural and bonding features of 72SnPO glass provide a very small Young’s modulus of \( E = 30 \) GPa. The Vickers hardness \( H_v \) at room temperature for 72SnPO glass in air was evaluated, in which the applied load was 25 g and the loading time 15 s. Figure 8 shows the optical photograph for the Vickers indentation pattern observed in 72SnPO glass. The cracking was appeared at the four corners of the indent. The Vickers hardness was evaluated to be \( H_v = 1.76 \) GPa. For the comparison, the Vickers indentation test was carried out for a phosphate glass, which is a commercially available phosphate glass with the composition of 42MgO.11Al2O3.47P2O5 (HOYAC500S), and the result is shown in Fig. 8. Any cracking was not observed under the load of 25 g, and the value of \( H_v = 5.24 \) GPa was evaluated. As reported by Kurkjian,41) many phosphate glasses have the values of \( H_v = 3-5 \) GPa, e.g., \( H_v = 3.85 \) GPa for 20SrO.10La2O3.70P2O5. Therefore, the Vickers indentation behavior shown in Fig. 8 indicates clearly that 72SnPO glass deforms very easily and is regarded as a brittle glass. As reported by Watanabe et al.,41) TeO2-based glasses, which are typical glasses showing a fragile character in the fragile/strong concept, have also small Vickers hardness, e.g., \( H_v = 2.6 \) GPa for 15Na2O.15ZnO.70TeO2. It is known that soda lime silicate glasses, which show a strong character, have the values of \( H_v = 5-6 \) GPa.41,42) e.g., \( H_v = 5.5 \) GPa for 15Na2O.10CaO.75SiO2.

As described in the introduction, it has been reported that 72SnPO glass works effectively as anode active materials for rechargeable lithium and sodium ion batteries.12-14) This suggests that Li+ ions and also Na+ ions can diffuse easily and fast into the structure of 72SnPO glass. In other words, the structure of 72SnPO glass might be largely open. Indeed, the present study supports this expectation. Furthermore, it is well known that almost all positive charge of Sn2+ ions in the anode of 72SnPO glass is compensated through electro-chemical reactions with lithium or sodium during the first charge process, consequently forming tin metal (Sn0) nano-scale particles (crystals).12,13) This behavior indicates that Sn2+ ions are easily reduced to Sn0. Because the glass transition temperature is low and the Young’s modulus is small, as demonstrated in this study, it is expected that the strength of Sn–O–P bonds would be weak. It is obvious that such weak bond strength would be favorable for the reducing reaction of Sn2+ ions to Sn0 metal particles.
5. Conclusions

A tin-phosphate glass with the composition of 72SnO·28P2O5 has been proposed as a promising candidate of new anode materials realizing lithium ion batteries. In order to clarify the features of the local structure and some physical/elastic properties of this glass, Raman scattering spectrum, 119Sn Mössbauer spectrum, thermal conductivity, Young’s modulus and Vickers hardness measurements were carried out. It was found that 72SnO·28P2O5 glass has an open structure with small thermal diffusivity and conductivity, small Young’s modulus, intense Boson peak, and small Vickers hardness, in which a large number of Q1 ((PO3.52B) and Q0 (PO43−) units are formed. A unique glass structure would be one of the main reasons for the fast diffusion of Li+ ions and result in the excellent battery performance of the glass.

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