Mechanical Properties of Ag^+/Na^+ Ion-exchanged Aluminosilicate Glasses

Fuji FUNABIKI*, Tetsuji YANO, Shuichi SHIBATA and Masayuki YAMANE

Department of Chemistry and Materials Science, Tokyo Institute of Technology, 2-12-1, O-okayama, Meguro-ku, Tokyo 152-8552

Mechanical properties of Ag^+/Na^+ ion-exchanged aluminosilicate glasses are investigated. The aluminosilicate glass samples with the thickness of 1 mm and homogeneous Ag^+/Na^+ concentrations were prepared via the ion exchange in the molten salt at 450°C and the following post-heating in the ambient atmosphere. Measured Young's modulus, Vickers hardness and fracture toughness in a dry nitrogen atmosphere change nonlinearly with increasing $\text{Ag}/(\text{Ag} + \text{Na})$ ratio, and show the maximum values, 75 GPa, 560 kg/mm² and 0.84 MN/m^{3/2} around $\text{Ag}/(\text{Ag} + \text{Na}) = 50\%$, respectively. Fully exchanged glass shows the same modulus 70 GPa as that of the mother glass and the smallest hardness and toughness, 500 kg/mm² and 0.74 MN/m^{3/2}, respectively. The calculated yield stress decreases from 2.59 GPa to 2.30 GPa with increasing $\text{Ag}/(\text{Ag} + \text{Na})$ at more than 60% region. Coexistence of Ag^+/Na^+ induces mixed cation effect, and gives a maximum to the elastic modulus at $\text{Ag} : \text{Na} = 1 : 1$. Additionally, the yield stress of glass is decreased with increasing Ag^+ concentration by the difference of the effect on Al–O–Si network between Ag^+ and Na^+ .

[Received January 18, 2007; Accepted May 17, 2007]

Key-words : Ion exchange, Silver, Mixed cation effect, Young's modulus, Vickers hardness, Fracture toughness, Yield stress

1. Introduction

Silver ion is known to be one of the ions having a high ionic mobility in glassy materials as well as alkali ions.^(1),2) Its unique electron configuration $[\text{Kr}]4d^{10}$ is considered to be an origin of this ionic transport property and also of its high electronic polarisability.⁽³⁾ Silicate glass system cannot contain a large amount of Ag^+ ions using melt-quench process owing to small Ag_2O solubility at high temperature, but using ion-exchange process like Ag^+/Na^+ . The ionic conductivity values of such Ag^+ -containing silicate glasses prepared via the ion exchange were reported to be 10^{-4} – 10^{-3} Scm⁻¹ at 200°C, which are one or two orders of magnitude larger than those of the mother glasses containing alkali ions.^(4),5) The choice of the initial silicate glasses which are free from non-bridging oxygen (NBO) enables us to prepare colorless ion-exchanged glasses, meaning that all silver can be introduced as ions without formation of metal colloids. However, other properties of these ion-exchanged glasses have not been examined well. Especially, the mechanical properties of Ag^+ -containing silicate glasses have been almost unknown. Only a few reports on Vickers indentation into the ion-exchanged layer of soda-lime-silica float glass can be found in the literatures^(6),7) because the examination of mechanical properties generally requires large homogeneous specimens.

Our group has examined the structure and properties such as glass transition temperature (T_g), thermal expansion coefficient (TEC), ionic transport, etc. of Ag^+/Na^+ ion-exchanged silicate glasses which had no concentration gradient of Ag^+ and Na^+ ions.^(4),5),8)–11) Monotonic decreases of T_g and TEC have been shown with increasing Ag_2O concentration in the ion-exchanged glasses. These have been reported in melt-quenched glasses of Ag_2O – Na_2O – B_2O_3 and Ag_2O – Na_2O – P_2O_5 glass systems too, which have large Ag_2O solubility at melting temperature different from silicate systems.^(12),13) However, the structural analysis showed that the large introduction of Ag^+ into Na_2O – SiO_2 glasses induced a crystallization of silicate network,^(8)–10) and that into Na_2O – TiO_2 – SiO_2 glasses induced an increase of oxygen coordination number of Ti^{4+} ions,⁽⁵⁾ while that into NBO-free Na_2O – Al_2O_3 – SiO_2 glasses only showed the shift of peak of Si–O–Al vibration in infrared spectra.⁽¹¹⁾ EXAFS analysis of Ag^+/Na^+ ion-

exchanged aluminosilicate glasses⁽¹⁴⁾ showed that the coordination number of Ag^+ ions in glasses was 2–3 much lower than that of alkali ions, 5–6. XPS analysis of Ag^+/Na^+ ion-exchanged silicate glasses⁽¹⁰⁾ also suggested the existence of Ag^+ ions coordinated with one NBO and one BO. Thus, during Ag^+/Na^+ ion exchange, remarkable changes of glass network structure have been observed, and it is considered that such difference of oxygen coordination number between the two ions induces certain structural strain in glasses and the following alternation or relaxation, as mentioned below too.

Ion exchange has been well utilized and investigated as a chemical strengthening of glass.⁽¹⁵⁾ Typical ion-exchange pair of K^+/Na^+ induces the residual compressive stress around the ion-exchanged layer due to the difference of ionic radius between K^+ and Na^+ . The size difference should require the glass network surrounding foreign ions to change its volume before and after the ion exchange. On the other hand, the difference of the ionic radius between Ag^+ and Na^+ is smaller than that between K^+ and Na^+ , and therefore, Ag^+/Na^+ ion exchange may not require the network to change its volume so much. However, it must require some transformation attributed to the difference of coordination number as mentioned above. It would be one of the origins of the structure changes and a decrease of T_g previously observed.

In this study, we prepared the homogeneously ion-exchanged aluminosilicate glasses with the thickness of 1 mm. They have various $\text{Ag}/(\text{Ag} + \text{Na})$ ratios from 0 to 100%. Their mechanical properties such as Young's modulus, Vickers hardness and fracture toughness were measured. From the obtained data, the effect of Ag^+/Na^+ ion exchange on Si–O–Al glass network is discussed.

2. Experiments

A sodium aluminosilicate glass of $25\text{Na}_2\text{O} \cdot 25\text{Al}_2\text{O}_3 \cdot 50\text{SiO}_2$ (in mol%) was prepared by a melt-quench method. The batch consisting of Na_2CO_3 , Al_2O_3 and SiO_2 was melted in a platinum crucible at 1650°C for one day. The melt was poured onto a carbon plate at room temperature, and transferred into an annealing furnace at 780°C. After holding it for 30 min, the sample was cooled at a rate of 5°C/min. The glass was cut into the pieces of 1 mm × 7 mm × 70 mm for Young's modulus

measurements, and those of 1 mm × 10 mm × 20 mm for Vickers indentation. The glass pieces were immersed in the eutectic molten salt of 65AgCl·35Ag₂SO₄ (in mol%) at 450°C for several periods of time varying from 30 min to 24 h. The gradient of the concentration profiles of Ag⁺ and Na⁺ were eliminated by the post heat-treatment at 450°C in ambient atmosphere for a few days. Some of the specimens were annealed again at $T_g + 20^\circ\text{C}$ for 30 min in order to eliminate a residual strain induced by the ion exchange.

The ion-exchange ratio of Ag/(Ag + Na) was determined by a spot analysis using energy dispersive X-ray spectroscopy equipped to a scanning electron microscope. T_g of the respective ion-exchanged samples was measured using a dilatometer at a heating rate of 5°C/min. Densities of the samples at room temperature were measured by Archimedes' method using water. Young's modulus was measured at room temperature by a vibration resonance method. For the sample length L , the thickness t and density ρ , Young's modulus E was determined using the following equation,

$$E = 0.9465 \times \frac{\rho f^2 L^4}{t^2} \times \left[1 + 6.59 \left(\frac{t}{L} \right)^2 \right]. \quad (1)$$

where the resonance frequency f was found by changing from 500 Hz to 1 kHz.

Vickers hardness was measured using micro-indenter. Indentations were carried out in an atmosphere with the relative humidity RH = 20–40% at room temperature with loads varying from 50 to 1000 g. Time period of the indentation was 15 s. 10 indentation points were made for one measurement condition. The diagonal length a and the depth d of impression of indenter were measured using a laser microscope with the accuracy of $\pm 0.5 \mu\text{m}$ and $\pm 0.1 \mu\text{m}$, respectively. Vickers hardness H_V was determined by the following equation,

$$H_V = \frac{2P \sin(68^\circ)}{a^2} = 1.854 \times \frac{P}{a^2}. \quad (2)$$

where P is the applied load. Elastic recover ratio, R_e , of the impression between on-loading and after-loading¹⁷⁾ was also calculated by the following equation,

$$\begin{aligned} R_e(\%) &= 100 \times \left(1 - 2\sqrt{2} \tan(68^\circ) \cdot \frac{d}{a} \right) \\ &= 100 \times \left(1 - 7.001 \times \frac{d}{a} \right). \end{aligned} \quad (3)$$

The fracture toughness was measured using indentation technique. The indentations were carried out in an ambient atmosphere or in a dry nitrogen gas at room temperature. The load was 1 kg and the time of the indentation was 15 s. The length of the median cracks outward from the impression corners was measured quickly using an optical microscope attached to the indenter. The fracture toughness K_c was calculated from the following equation given by Lawn et al.,¹⁷⁾

$$K_c = 0.016 \times \left(\frac{E}{H_V} \right)^{1/2} \frac{P}{c^{3/2}}. \quad (4)$$

where c is a half of the length of radial crack.

3. Results

All the ion-exchanged samples were transparent and crack-free. The formation of silver colloid was not observed in the glasses. **Figure 1** shows the thermal expansion curves of the samples with various Ag/(Ag + Na) ratios. The glass transition temperature T_g decreased from 760°C to 650°C with

Fig. 1. Thermal expansion curves of the ion-exchanged glasses before and after annealing.

Fig. 2. Plots of the density and molar volume of the ion-exchanged glasses as a function of the ion-exchange ratio. The circles represent the density, and the triangles represent the molar volume. The closed symbols represent the values before annealing, and the opened ones represent the values after annealing.

increasing the ion-exchange ratio Ag/(Ag + Na). The expansion traces of the samples before annealing showed certain shoulder around 600°C, but they disappeared after the annealing at $T_g + 20^\circ\text{C}$ as shown at the bottom trace of the sample with Ag/(Ag + Na) = 100%.

Figure 2 shows the density and the calculated molar volume of the samples as a function of Ag/(Ag + Na) ratio. The density was linearly increased from 2.497 g/cm³ to 3.850 g/cm³ by the full ion-exchange treatment. The molar volume was increased in the degree of about 3%. The annealing of samples decreased the molar volume in the degree of about 0.2% as same as the change of the sample length as shown in **Fig. 3**.

Figure 4 shows Young's modulus E of the ion-exchanged glasses before and after annealing. Calculated Young's modulus values were also plotted, which are derived using the equation given by Makishima et al.¹⁸⁾ The measured values

Fig. 3. Increasing ratio of the sample length of the ion-exchanged glasses before and after annealing. The closed symbols represent the values before annealing, and the opened ones represent the values after annealing.

Fig. 5. Plots of Vickers hardness of the ion-exchanged glasses as a function of the ion-exchange ratio. The closed circles represent the values before annealing, and the opened ones represent the values after annealing.

Fig. 4. Plots of Young's modulus of the ion-exchanged glasses as a function of the ion-exchange ratio. The closed circles represent the values before annealing, and the opened ones represent the values after annealing. The dashed line represents the values calculated using the equation given by Makishima et al.¹⁸⁾

increased monotonically from 70 GPa to 75 GPa with increasing $\text{Ag}/(\text{Ag}+\text{Na})$ up to 40%, and then, decreased to 70 GPa. The annealing caused the slight increases at high $\text{Ag}/(\text{Ag}+\text{Na})$ region. On the other hand, the calculated E values showed a contrary trend compared with the measured ones.

Figure 5 shows Vickers hardness of the ion-exchanged glasses before and after annealing. The hardness of the unannealed glasses decreased monotonically from 548 kg/mm^2 to 475 kg/mm^2 with increasing $\text{Ag}/(\text{Ag}+\text{Na})$ ratio, while the hardness of the annealed ones showed higher values than those of the unannealed ones and a maximum around $\text{Ag}/(\text{Ag}+\text{Na}) = 40\%$. **Figure 6** shows the elastic recover ratio R_e of the annealed ion-exchanged glasses. The increase of $\text{Ag}/(\text{Ag}+\text{Na})$ ratio decreases R_e slightly.

Fig. 6. Plots of the elastic recovery ratio of the impressions on the annealed ion-exchanged glasses.

$\text{Na})$ ratio decreases R_e slightly.

Figure 7 shows the fracture toughness K_c of the annealed ion-exchanged glasses measured in a dry nitrogen gas. K_c exhibited a maximum value of 0.84 $\text{MN}/\text{m}^{3/2}$ around $\text{Ag}/(\text{Ag}+\text{Na}) = 50\%$. The fully exchanged glass had the smallest value $K_c = 0.74 \text{ MN}/\text{m}^{3/2}$.

4. Discussion

4.1 Structural relaxation in NBO-free ion-exchanged glasses

Sodium aluminosilicate glass used in this study contains no non-bridging oxygen (NBO) because this glass satisfies the atomic ratio of $\text{Na}/\text{Al} = 1$.¹⁹⁾ Additionally, it has been concluded that Ag^+/Na^+ ion exchange treatment generates no NBO in this glass.¹¹⁾ Therefore, the structure of the ion-exchanged aluminosilicate glasses holds three-dimensional

Fig. 7. Plots of the fracture toughness of the annealed ion-exchanged glasses measured in a dry nitrogen gas.

network consisting of Al–O–Si bonds. The observed small shoulders of the thermal expansion traces of the unannealed ion-exchanged samples (Fig. 1) are considered to indicate that their three-dimensional networks shrink beyond the strain point. Additionally, the observed increases of the glass volume and sample length during ion exchange (Fig. 2 and 3) are considered to be the expansion of Al–O–Si network of mother glass due to the introduction of large foreign ions, and the following slight decreases during annealing are considered to be the shrink of Al–O–Si network due to certain atomic adjustment. Previously, Shaisha et al.²⁰⁾ reported that Ag⁺/Na⁺ ion exchange induces a relatively small compressive stress on the glass surface compared with other alkali ion-pairs because of the small difference of the ionic radius between Ag⁺ and Na⁺. This difference of the ionic radius would increase the volume of mother glass. Furthermore, as reported by Houde-Walter et al.,¹⁴⁾ these ions have quite different coordination number in the aluminosilicate glasses each other. So NBO-free ion-exchanged glasses would be hard to release an induced structural strain owing to the difference of coordination number at the ion-exchange temperature of 450°C below the glass transition temperature T_g , it would be reasonable to consider that the structural shrink during annealing indicates the occurrence of the structural relaxation centering Ag⁺ ions. This relaxation would change the bond distances and angles of Al–O–Si network, and would be one of the reasons for the observations that the mechanical properties of ion-exchanged glasses increased during annealing.

4.2 Mixed cation effects of ion-exchanged glasses

The nonlinear changes of glass properties due to mixing of modifier oxides in glass have been widely discussed by many authors.^{21)–23)} When the different kinds of alkali oxides coexist in glass, ionic conductivity is known to decrease and show a minimum at a certain mixing ratio.²⁴⁾ Ag⁺/Na⁺ ion-exchanged glass samples with homogeneous ion distribution in the glass samples were investigated by author's group.^{4),5)} They have an ionic conductivity minimum at certain Ag/(Ag + Na) ratio as well as the melt-quenched mixed alkali glasses. Mixed cation effects of the mechanical properties shown in Figs. 4, 5 and 7 are the first observations on the homogeneously ion-exchanged glass samples, and it is noteworthy to compare the previous mixed cation effect on the mechanical

properties of the melt-quenched glasses.^{25)–28)} The mixed cation effect on Young's modulus observed in this study is estimated at an increase of 7%, and this degree is nearly equal to increases of 5–10% observed in melt-quenched mixed alkali silicate glasses. This implies that there is some characteristic difference between Ag⁺ and Na⁺ as similar to alkali ion-pairs having large difference in ionic radius.

Compositional dependence of Young's modulus of the melt-quenched glasses has been investigated by Makishima et al.¹⁸⁾ They proposed the equation to predict Young's modulus from the glass composition;

$$E = 2 \frac{\rho_g}{M} \sum (V_i x_i) \sum (G_i x_i). \quad (5)$$

where ρ_g , M , X_i , V_i and G_i are the density of glass, the molecular weight of glass, the molar fraction, the ionic volume and the dissociation energy per unit volume of consisting oxide i , respectively. In calculation of Young's modulus of Ag⁺/Na⁺ ion-exchanged glasses, the measured densities ρ_g (Fig. 2) and the values of V_i and G_i given by Inaba et al.²⁹⁾ were used. In Fig. 4, the calculated values are shown by a broken line. These show different trends against Ag/(Ag + Na) ratio, and Eq. (5) fails to predict Young's modulus of Ag⁺/Na⁺ ion-exchanged aluminosilicate glasses; a minimum is found in the calculated Young's modulus while a maximum in the measured one. The appearance of a minimum in calculated one is caused by the change of ρ_g/M in the equation. There is also a large gap of about 10 GPa between measured modulus and calculated one, which is in the allowable error of this equation. On the other hand, we see a good agreement that Young's modulus of the fully exchanged glass is almost equal to that of the initial glass because $V(13.6 \text{ cm}^3/\text{mol})$ and $G(27.2 \text{ kJ/cm}^3)$ of Ag₂O are near to those of Na₂O, $11.2 \text{ cm}^3/\text{mol}$ and 31.9 kJ/cm^3 , respectively. It implies that the degree of the effect of Ag₂O on an elastic deformation of glass is theoretically equal to that of Na₂O. Previously, author's group reported the ionic conductivity of Ag⁺/Na⁺ ion-exchanged NBO-free aluminosilicate glasses, and mixed mobile ion effect (MMIE) was observed to occur at Ag/Na = 1 not only in the conductivity but also in the activation energy of ionic conduction. Anderson et al.³⁰⁾ proposed an equation of activation energy of ionic conduction E_σ correlating with the elastic property of matrix materials.

$$E_\sigma = \frac{\beta z z_o e^2}{\gamma (r + r_o)} + 4\pi S r_D (r - r_D)^2. \quad (6)$$

where β , z , z_o , γ , S , r , r_o and r_D are the finite displacement factor, the valence number of mobile cation, that of oxygen ion, the polarisability of oxygen ion, the shear modulus of glass matrix, the ionic radius of mobile cation, that of oxygen ion and the radius of the cavity in the network, respectively. A–S model is based on the movement of the mobile ions that migrate through the glass by expanding the surrounding network. For the isotropic materials like glass, there is the correlation between E and S as

$$S = \frac{E}{2(1-\nu)}. \quad (7)$$

where S and ν are the shear modulus and the Poisson's ratio, respectively. If the Poisson's ratio ν is independent of the ion-exchange ratio, the increase of Young's modulus increases the activation energy of ionic conduction, E_σ through the increase of S .

Makishima et al.³¹⁾ reported the Poisson's ratio ν of glass as a function of the packing density V obtained from the molar

Fig. 8. Plots of Poisson's ratio and the shear modulus of the annealed ion-exchanged glasses calculated. The closed circles represent Poisson's ratio. The opened ones represent the shear modulus.

volume and ionic radii of the consisting elements as the following equation;

$$\nu = 0.5 - \frac{1}{7.2V}. \quad (8)$$

Using these equations, the Poisson's ratio of the Ag⁺/Na⁺ ion-exchanged aluminosilicate glasses can be calculated as shown in Fig. 8. They were in the narrow range of 0.21 ± 0.01 , and are considered to be almost independent of the ion-exchange ratio. Therefore, Eq. (7) would give the same dependence of the shear modulus S on the Ag/(Ag+Na) as Young's modulus E ; S shows a maximum around Ag/(Ag+Na) = 50%, and there is no remarkable difference of S between the initial glass and fully exchanged glass as shown in Fig. 8. This means that the ionic conductivity of ion-exchanged glass samples show a mixed mobile ion effect (MMIE) due to the mixed cation effect of shear modulus S if the obtained S from Eq. (7) is adaptable to A-S model. In practice, the activation energy E_a of the ionic conductivity of Ag⁺/Na⁺ ion-exchanged aluminosilicate glasses shows a maximum at Ag/(Ag+Na) = 50%, and there is no remarkable difference of E_a between the initial glass and fully exchanged glass.⁴⁾ In this meaning, the mechanical properties surely has a large influence on the ionic conductivity as predicted by A-S model, and the mixing of cations prohibits the displacement of the mobile ion to the neighboring vacant site by expanding the gate of oxygen ions. The nonlinear change of elastic modulus of glass network would affect on the plastic deformation of the three dimensional network of glass, where bond breaking by stress dominates the brittleness and toughness of glass. It is discussed in the next section.

4.3 Plastic deformation of ion-exchanged glasses

Indentation onto the glass surface causes the elastic deformation and the plastic one in the glass structure. The former deformation was evaluated as shown in Fig. 6, and its degree to the total deformation (37–40%) was smaller than that of the latter one (60–63%). Generally, plastic deformation is considered to consist of densification, slipping deformation and pulling one. In NBO-free aluminosilicate glass, the densification is the compaction of tetrahedral units of SiO₄ and

Fig. 9. Plots of the yield stress Y and $\lambda/a_0^{1/2}$ of the annealed ion-exchanged glasses calculated. The closed circles represent the yield stress. The opened ones represent $\lambda/a_0^{1/2}$. The small figure shows the change of Y/E against the ion-exchange ratio.

AlO₄, and the slipping deformation is the shear flow of these units through the breaking of Al–O–Si bonds, while the pulling one is the atomic breaking between the two units. Transition point from elastic deformation to plastic one is called yield point. We consider that the yield stress of NBO-free aluminosilicate glass represents the resistance of Al–O–Si network to the three plastic deformations in glass. According to Marsh,³²⁾ the yield stress Y of glass is given by

$$\frac{H_V}{Y} = C + K \frac{3}{3-\lambda} \ln \frac{3}{\lambda + 3\mu - \lambda\mu}. \quad (9)$$

where H_V is Vickers hardness of glass, $C = 0.28$, $K = 0.6$, $\lambda = (1 - 2\nu)Y/E$, $\mu = (1 + \nu)Y/E$. The yield stress of the annealed glass samples is calculated as shown in Fig. 9. Y is almost constant 2.59 GPa at $0 < \text{Ag}/(\text{Ag} + \text{Na}) < 60\%$, and then decreases to 2.30 GPa for the fully exchanged glass sample. On the other, we treat a parameter of Y/E . The ratio of Y/E is considered to indicate the minimum strain of Al–O–Si network to be broken. In Fig. 9, Y/E decreases monotonically with increasing Ag/(Ag+Na) ratio. These changes suggest that Y contains two changes on Ag/(Ag+Na); one is a maximum change due to mixed cation effect through the elastic modulus of glass, and the other is a change not concerning with mixed cation effect, but Ag⁺ concentration. The monotonic decrease against Ag/(Ag+Na) is similar with the change of T_g ,¹¹⁾ and Ag⁺ ion seems to decrease the interaction range of Al–O–Si network in proportion to its concentration in glass.

On the other hand, fracture toughness is a parameter for the resistance of bonds to pulling deformation. The following equation is given for the fracture toughness K_{IC} .

$$K_{IC} = \left(\frac{2E\gamma_f}{1-\nu^2} \right)^{1/2} = \left(\frac{\lambda \sqrt{2}}{\pi a_0^{1/2} (1-\nu^2)^{1/2}} \right) E. \quad (10)$$

where γ_f , λ and a_0 are the fracture surface energy, the range of inter-atomic forces and the inter-atomic spacing, respectively. From the measured K_{IC} and E , the calculated $\lambda/a_0^{1/2}$ are plotted in Fig. 9. The K_{IC} divided by E , the value of $\lambda/a_0^{1/2}$ decreased gradually with increasing Ag/(Ag+Na) ratio. Its trend resembles well with the change of Y/E . In the annealed ion-

exchanged glass samples, Ag^+ and Na^+ are considered to occupy the sites where the surrounding oxygen atoms and local network are relaxed to match the characteristics of the respective cations,³³⁾ but there is still no NBO in the structure.¹¹⁾ Therefore, the decrease of $\lambda/a_0^{1/2}$ is considered to represent the change of the bond distance or angle of Al–O–Si bond depending on the fraction of Ag^+ and Na^+ in the glasses. Lower oxygen coordination number of Ag^+ than those of Na^+ should be considered again to give explanations to the decreases of Y/E and $\lambda/a_0^{1/2}$. When the dissociation energies per mole of Ag_2O and Na_2O are compared, there is only slight difference between them; $G(\text{Ag}_2\text{O}) = 907 \text{ kJ/mol}$, $G(\text{Na}_2\text{O}) = 936 \text{ kJ/mol}$.²⁹⁾ From these energies, the bond strength of Ag–O and Na–O can be calculated by dividing by the oxygen coordination number. Larger bond strength of Ag–O than Na–O might be contradictory to the decreases of Y/E and $\lambda/a_0^{1/2}$ with the increase of $\text{Ag}/(\text{Ag} + \text{Na})$ ratio. However, the two-oxygen coordination of Ag^+ means that Ag–O is highly directional bonds compared with Na–O. In the deformation process, the weak bonds of the glass structure, Ag–O and Na–O, are firstly elongated and broken followed by the breakage of Al–O–Si bonds in the ion-exchange glass samples. Since the bonds of Ag–O and Na–O are considered to act as the bridges reinforcing the three-dimensional network, the breaking of these bonds affects much on the plastic deformation mechanism. Low coordination number of Ag^+ ions in aluminosilicate glasses¹⁴⁾ suggests that the breaking of one of two bonds easily cause the catastrophic breakage of the network structure, while Na–O bonds have weak but highly coulomb interactions to all directions. Large coordination number of Na^+ ions might relieve the substantial elongation of Al–O–Si bonds. It is considered that the gradual decreases of Y/E and $\lambda/a_0^{1/2}$ found in Ag^+/Na^+ ion-exchanged aluminosilicate glasses are originated in the local structure of Ag^+ and Na^+ ions in the NBO-free glasses.

5. Conclusion

The effect of Ag^+/Na^+ ion exchange on Al–O–Si glass network was investigated from the point of view of mechanical properties of Young's modulus, Vickers hardness and fracture toughness. It was found that Young's modulus, Vickers hardness and fracture toughness became maximum at the ion exchange ratio of $\text{Ag}/(\text{Ag} + \text{Na}) = 50\%$ because of the mixed cation effect between Ag^+ and Na^+ . The calculated shear modulus also showed the mixed cation effect, clarifying the strong correlation between the mixed cation effect of mechanical properties and the mixed mobile ion effect of the ionic conductivity. The calculated yield stress showed an almost constant value at $0 < \text{Ag}/(\text{Ag} + \text{Na}) < 60\%$ and decreased in $60 < \text{Ag}/(\text{Ag} + \text{Na}) < 100\%$. From the structural data in the literatures, the effects of the local structures of Ag^+ and Na^+ ions were discussed to give the explanations to the observed mechanical behaviors, and the characteristic differences between Ag^+ and Na^+ ions are considered to be a key factor to govern their mechanisms.

References

- 1) Toda, K., Suzuki, T. and Sato, M., *Solid State Ionics*, Vol. 93, pp. 177–181 (1997).
- 2) Daidouh, A., Veiga, M. L. and Pico, C., *J. Solid State Chem.*, Vol. 130, pp. 28–34 (1997).
- 3) Duffy, J. A., Harris, B., Kamitsos, E. I., Chrysikos, G. D. and Kapoutsis, J. A., *Phys. Chem. Glasses*, Vol. 39, pp. 275–280 (1998).
- 4) Yano, T., Nagano, T., Lee, J., Shibata, S. and Yamane, M., *Solid State Ionics*, Vol. 150, pp. 281–290 (2002).
- 5) Funabiki, F., Yano, T., Shibata, S. and Yamane, M., *Solid State Ionics*, Vol. 160, pp. 281–288 (2003).
- 6) Odo, G. Y., Nogueira, L. N. and Lepienski, C. M., *J. Non-Cryst. Solids*, Vol. 247, pp. 232–236 (1999).
- 7) Suszynska, M., Szmida, M. and Grau, P., *Mater. Sci. Eng.*, Vol. A319–321, pp. 702–705 (2001).
- 8) Takada, H., Yano, T., Yasumori, A., Shibata, S. and Yamane, M., *Ceram. Trans.*, Vol. 30, pp. 181–187 (1993).
- 9) Yamane, M., Shibata, S., Yasumori, A., Yano, T. and Takada, H., *J. Non-Cryst. Solids*, Vol. 203, pp. 268–273 (1996).
- 10) Yano, T., Azegami, K., Shibata, S. and Yamane, M., *J. Non-Cryst. Solids*, Vol. 222, pp. 94–101 (1997).
- 11) Yano, T., Nagano, T., Lee, J., Shibata, S. and Yamane, M., *J. Non-Cryst. Solids*, Vol. 270, pp. 163–171 (2000).
- 12) Boulos, E. N. and Kreidl, N. J., *J. Am. Ceram. Soc.*, Vol. 54, pp. 368–375 (1971).
- 13) Bartholomew, R. F., *J. Non-Cryst. Solids*, Vol. 12, pp. 321–332 (1973).
- 14) Houde-Walter, S. N., Inman, J. M., Dent, A. J. and Greaves, G. N., *J. Phys. Chem.*, Vol. 97, pp. 9330–9336 (1993).
- 15) Nordberg, M. E., Mochel, E. L., Garfinkel, H. M. and Olcott, J. S., *J. Am. Ceram. Soc.*, Vol. 47, pp. 215–219 (1964).
- 16) Ziemath, E. C. and Hermann, P. S. P., *J. Non-Cryst. Solids*, Vol. 273, pp. 19–24 (2000).
- 17) Lawn, B. R., Evans, A. G. and Marshall, D. B., *J. Am. Ceram. Soc.*, Vol. 63, pp. 574–581 (1980).
- 18) Makishima, A. and Mackenzie, J. D., *J. Non-Cryst. Solids*, Vol. 12, pp. 35–45 (1973).
- 19) Onorato, P. I. K., Alexander, M. N. and Struck, C. W., *J. Am. Ceram. Soc.*, Vol. 68, C148–150 (1985).
- 20) Shaisha, E. E. and Cooper, A. R., *J. Am. Ceram. Soc.*, Vol. 64, pp. 278–283 (1981).
- 21) Klonkowski, A., *J. Non-Cryst. Solids*, Vol. 57, pp. 339–353 (1983).
- 22) Habasaki, J., Okada, I. and Hiwatari, Y., *J. Non-Cryst. Solids*, Vol. 183, pp. 12–21 (1995).
- 23) Kirchheim, R., *J. Non-Cryst. Solids*, Vol. 272, pp. 85–102 (2000).
- 24) Isard, J. O., *J. Non-Cryst. Solids*, Vol. 1, pp. 235–261 (1969).
- 25) Yamane, M., Fujita, Y. and Sakaino, T., *J. Mater. Sci. Soc. Jpn*, Vol. 11, pp. 156–157 (1974).
- 26) Matusita, K., Sakka, S., Osaka, K., Soga, N. and Kunugi, M., *J. Non-Cryst. Solids*, Vol. 16, pp. 308–312 (1974).
- 27) Karapetyan, G. O., Lifshits, V. Ya., Kemilov, S. V. and Tennison, D. G., *Fiz. Khim. Stekla*, Vol. 10, pp. 567–574 (1984).
- 28) Salama, S. N. and El-Batal, H. A., *J. Non-Cryst. Solids*, Vol. 168, pp. 179–185 (1994).
- 29) Inaba, S., Fujino, S. and Morinaga, K., *J. Am. Ceram. Soc.*, Vol. 82, pp. 3501–3507 (1980).
- 30) Anderson, O. L. and Stuart, D. A., *J. Am. Ceram. Soc.*, Vol. 37, pp. 573–580 (1954).
- 31) Makishima, A. and Mackenzie, J. D., *J. Non-Cryst. Solids*, Vol. 17, pp. 147–157 (1975).
- 32) Marsh, D. M., *Proc. Roy. Soc.*, Vol. A279, pp. 420–435 (1963).
- 33) Dubiel, M., Brunsch, S., Kolb, U., Gutwerk, D. and Bertagnolli, H., *J. Non-Cryst. Solids*, Vol. 220, pp. 30–44 (1997).