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ION-EXCHANGE-INDUCED CRYSTALLIZATION OF A GLASS BELOW T_g

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Introduction

Ion exchange between glass and molten silver salt is often used as a technique for introducing silver ions into the glass to obtain high performance optical materials, such as gradient-index glasses [1, 2].

In studying the Ag^+/Na^+ ion exchange process in sodium silicate glass, the authors found that the precipitation of $Ag_{10}Si_4O_{13}$ crystal in the glass was induced by soaking the initial glass at a temperature well below its glass transition temperature, T_g . This is quite unusual. No paper describes this unusual structural evolution of the glass during the ion exchange process, because most basic studies on Ag^+/Na^+ ion exchange are mainly concerned with diffusion [3-6]. Only a few papers reported the formation of Ag colloid in highly silver-doped glasses accomplished with reducing agent or reduction procedures [7, 8]. In this work, structural evolution of the glass during ion exchange was investigated in order to understand such a unique crystallization phenomena induced by ion exchange.

Experimental

A sodium silicate glass of the composition 25 Na_2O -75 SiO_2 (mol%) was obtained by melting. The batch materials consisting of reagent grade SiO_2 and Na_2CO_3 was melted in a platinum crucible at $1500^\circ C$ for 2hrs. The glass, once being pulverized to size below about 0.5mm, was remelted at $1500^\circ C$ for 1h to improve homogeneity. The 25x15x0.5mm platelet glass prepared after remelting was subjected to ion exchange by soaking in a 40g molten $AgNO_3$ bath being contained in a high silica glass crucible at $365^\circ C \pm 2^\circ C$. This temperature is about $100^\circ C$ below the glass transition temperature of the initial sodium silicate glass. The soaking time in the molten salt was changed

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from 1 to 48hrs.

For the purpose of investigating the structure and properties of glasses containing various Ag contents, some of the glasses were further subjected to heat-treatment at 365°C in ambient atmosphere to equalize the Ag concentration within the glasses. These glasses are denoted hereafter as Ag-equalized glasses and those without this treatment are denoted as ion-exchanged glasses. The total time for soaking in molten salt and for heating in air was fixed at 48hrs.

The concentration profile of Ag⁺ ions in both ion-exchanged and Ag-equalized glasses were determined from spot analysis by energy dispersive spectroscopy (EDX). The development of crystallization was investigated by X-ray diffraction (XRD) and small angle X-ray scattering (SAXS) measurements. The morphology of the crystal was observed by scanning electron microscopy (SEM). The change in the local structure of the glass network with ion exchange was investigated by micro infrared reflectance spectroscopy (IRRS) measurement in the range from 4000 to 700cm⁻¹. The glass transition temperature of the Ag-equalized samples, which maybe a reflection of the structural change due to Ag⁺ substitution for Na⁺ ions, was measured by dilatometry. The 10.5x3x0.3mm rectangular glass samples supported by silica glass plate were prepared and supplied for the measurement.

Results

Concentration profiles along the thickness direction in the ion-exchanged and Ag-equalized glasses are shown in Fig. 1(a) and (b), respectively. The depth of the ion exchanged layer increased with increasing soaking time. After 24hrs of soaking, no Ag concentration gradient remained. The Ag₂O content reached 25mol% in replacement for 25mol% of Na₂O in the initial glass. No change in Ag concentration occurred for the glass soaked for 48hrs. All Ag-equalized glasses had uniform Ag concentration profiles, with particular levels depending on the soaking time.

The XRD patterns from the original surfaces and polished surfaces down to a depth of 0.1mm of ion-exchanged glasses are shown in Fig. 2(a) and (b), respectively. In Fig. 2(a), the diffraction angle giving a halo already shifted from about 25 to 33 degrees after soaking for 1h. Broad peaks due to Ag₁₀Si₄O₁₃ appeared from the sample soaked for 3hrs and increased in intensity with time. However, Fig. 2(b) shows that no peak was observed from the interiors of sample soaked for 36hrs. Therefore, it is concluded that crystallization rapidly occurred near the surface with little extension in to the interior.

The SEM micrographs of the cross-section of the ion-exchanged sample soaked for 48hrs is shown in Fig. 3. It is known that the submicron-size crystals are spheroids and that the nucleation sites are not on the surface but inside the glass. No such particles were observed in samples soaked up to 30hrs.

On the contrary, results of the SAXS measurements for ion-exchanged glass after polishing to a depth of 0.1mm were different depending on the soaking time. The sample soaked for 12hrs already exhibited strong scattering, whereas the sample soaked for 3 hrs

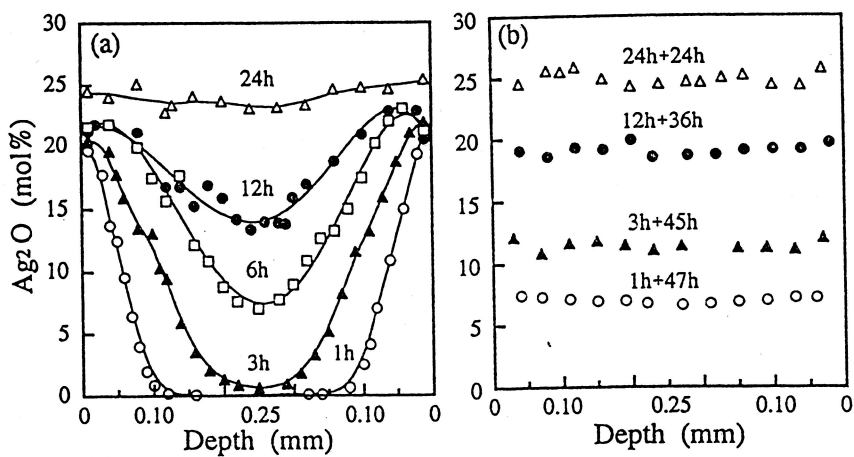


Figure 1 Concentration profiles of Ag_2O ;

(a) Ion-exchanged glass.

(b) Ag-equalized glass.

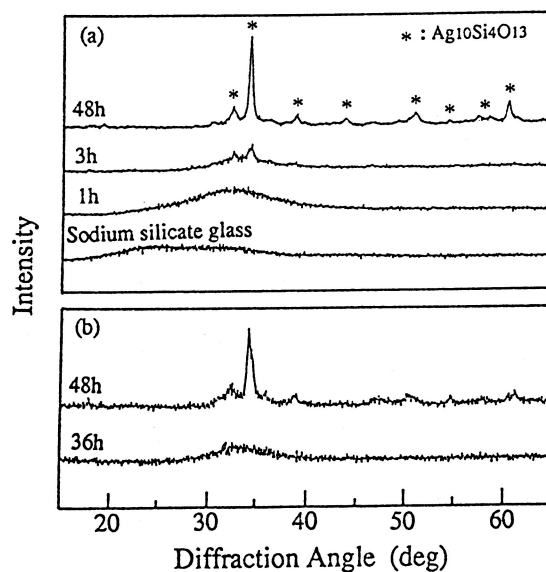
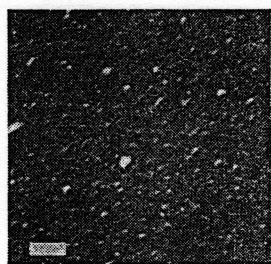


Figure 2 XRD patterns from (a) original and (b) polished surfaces of ion-exchanged glass.

exhibited minimal scattering. Estimated size of the scattering particles from the well-known Guinier plot was about 300Å in diameter. This indicates that the scattering particles had formed in the glass far before the crystallization became appreciable inside the glass.

The T_g of Ag-equalized glasses decreased monotonically with increasing Ag concentration, as shown in Fig. 4. The T_g of the 25mol% Ag_2O glass was about 270°C, which is 200°C below the T_g of original sodium silicate glass. This enormous decrement in T_g signifies that the Ag^+ ions did not simply replace for the Na^+ ions, but that this replacement significantly affected the strength of glass structure and/or modified the structure itself. The decrement of T_g due to Ag^+/Na^+ ion exchange was also reported in sodium aluminosilicate glasses [6].



(white bar = 1 μm)

Figure 3 SEM photograph of the cross section of ion-exchanged glass soaked for 48h.

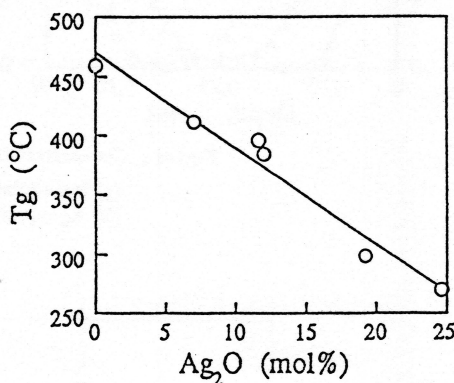


Figure 4 Glass transition temperature of Ag-equalized glass as a function of Ag concentration.

Figure 5 shows the dielectric loss curves for the (a) ion-exchanged and (b) Ag-equalized samples calculated from IRRS curves by using Kramers-Kronig transformation. The maxima of the dielectric loss curves are coincident with those of the absorption coefficient [9]. The numbers in parentheses in Fig. 5(a) are the depths of measured areas from the initial surface. The Ag concentration in measured area estimated from Ag concentration profile are also noted.

Two maxima on the curve for the original sodium silicate glass are attributed to the Si-O-Si (or bridging oxygen) bonds at 1050 cm^{-1} and the Si-O-modifier (or non-bridging oxygen) bonds at 980 cm^{-1} . The curves for low Ag content Ag-equalized glasses had a single peak which shifted towards higher wavenumbers as Ag concentration increased. The curve for the sample soaked for 24hrs and equalized for 24hrs had two maxima again at around 1060 cm^{-1} and 1000 cm^{-1} . Curves for ion-exchanged glasses were similar to those for Ag-equalized glass containing similar amount of Ag, except for the sample soaked for 48hrs which had a single peak at around 1080 cm^{-1} .

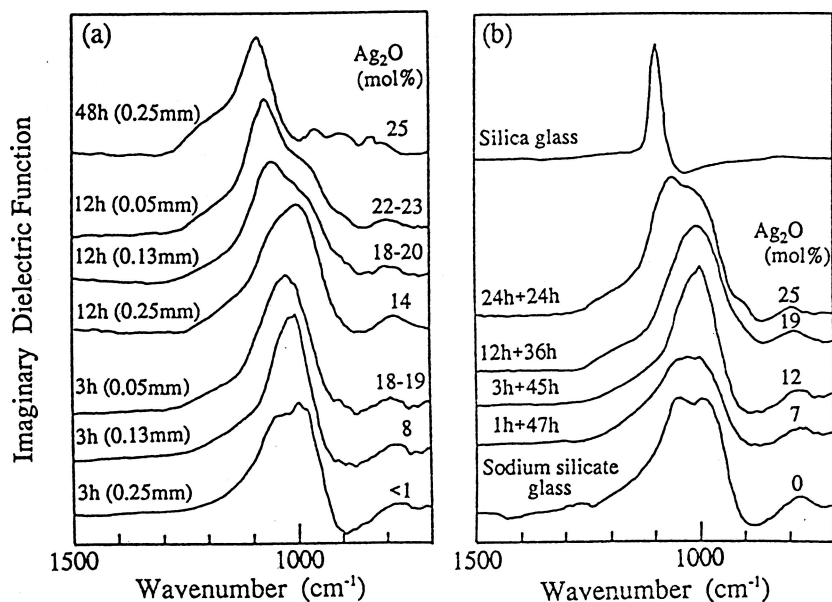


Figure 5 Dielectric loss curves of (a) ion-exchanged and (b) Ag-equalized samples.

Discussion

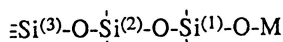
Results of T_g measurements indicate that the temperature of ion exchange and of heat-treatment becomes higher than T_g , for the glass with more than 13mol% Ag_2O . Therefore, such heat-treatment above T_g can enhance structural change in the glass matrix. This is perhaps the reason for crystallization below T_g of the initial glass. In order to clarify the structural evolution of the glass during ion exchange, the effect of Ag^+ ions on glass structure should be understood.

Well-known is the high diffusion coefficient of Ag^+ ions and its selective incorporation into the glass during ion-exchange, as compared to alkali ions [10, 11]. Such high diffusivity and selectivity of Ag^+ ions are attributed to their strong polarizing power [10] or acidity [11]. Experimentally, the polarizability of alkali aluminosilicate and soda-lime silicate glasses was found to increase with Ag^+ ion concentration [3]. The cause of such peculiarities of Ag^+ ions during ion-exchange process is considered to be an important issue for explaining the structural change which induced the unique crystallization in this study.

In order to understand the structural evolution during ion-exchange, the character of the $\equiv Si-O-Ag$ bond in the glass network should be considered. The electronegativity of

Ag⁺ ion is more than twice that of alkali (M) ions, so that the Ag-O bond is more covalent than the M-O bonds. From electronegativity theory, the percentage of ionic character in the Ag-O bond is much lower than that of the M-O bonds. These percentages are as follows: 42% for Ag-O, 79% for Li-O, 82% for Na-O, and 84% for K-O bonds. This more covalent character in the Ag-O bond agrees with the strong polarizing power of Ag⁺ ion, as noted previously.

The influence of the polarizing power of a single-valent cation M in the silica network can be apparent by considering the following schematic:



The M-O bond affects not only the $\equiv\text{Si}^{(1)}-\text{O}$ bond but also the $\equiv\text{Si}^{(2)}-\text{O}-\text{Si}^{(1)}\equiv$ and the $\equiv\text{Si}^{(3)}-\text{O}-\overset{\cdot}{\underset{\cdot}{\text{Si}}}^{(2)}-\text{O}-$ bonds. When M is an alkali ion, T_g of the alkali silicate glass decreases when it contains alkali ions in order of K⁺, Na⁺ and Li⁺. This suggests that the $\equiv\text{Si}-\text{O}-\text{Si}\equiv$ bonding becomes weaker as the M-O bonding becomes more covalent. In light of the above calculations, Ag⁺ ions introduced into the glass network would lower T_g due to their strong polarizing power. Indeed, this rationale was consistent with our results shown in Fig. 4.

In Fig. 5, the single peak on both curves of the ion-exchanged and Ag-equalized samples containing about 12mol% Ag₂O is positioned between the two maxima of the initial glass in the range of 1010-1020cm⁻¹. This seems to indicate that most of the $\equiv\text{Si}-\text{O}-\text{Si}\equiv$ bonds were affected and weakened by the Ag-O bonds, so that the peak of the $\equiv\text{Si}-\text{O}-\text{Si}\equiv$ bond shifted towards lower wavenumbers. This structural change in the glass network is coincident with the shifting of the halo on the XRD patterns during the early stage of ion-exchange.

Broadening of the peaks occurred on the dielectric loss curves of the centers of the ion-exchanged sample soaked for 12hrs (14mol% Ag₂O) or of the Ag-equalized 12hrs+36hrs sample (19mol% Ag₂O). Curves of the surface of the same ion-exchanged sample or Ag-equalized 24hrs+24hrs sample showed two maxima at around 1060cm⁻¹ and 1000cm⁻¹. However, after soaking for 48hrs, curve changed to a single peak with position very close to that of silica glass in Fig. 5(b). These results indicate that the rigid $\equiv\text{Si}-\text{O}-\text{Si}\equiv$ bonds were reformed by heat-treatment above T_g. The SAXS results (after soaking for 12hrs) suggest the existence of SiO₂-rich and Ag-rich portions in the glass through the formation of the rigid $\equiv\text{Si}-\text{O}-\text{Si}\equiv$ bond.

These phenomena can be understood since Ag⁺ ions do not simply substitute for Na⁺ ions but attack the weakened $\equiv\text{Si}-\text{O}-\text{Si}\equiv$ bonds in the vicinity of the Ag-O bonds to form another Ag-O bond. In that case, the $\equiv\text{Si}-\text{O}-\text{Si}\equiv$ bond is formed in another place by the Na⁺ ion diffusion to maintain charge balance in the glass matrix. The SiO₂-rich and Ag-rich portions were formed by such a structural change, thereby allowing the Ag-rich portions to change into crystals by further heat-treatment above T_g.

In summary, Ag⁺ ions introduced into the glass network lowered T_g and formed SiO₂- and Ag-rich portions due to the strong polarizing power of Ag⁺ ions. Thus, this is

considered to be the cause of the crystallization phenomena of a glass below the T_g of the initial glass.

Reference

1. S. Ohmi, H. Sakai, Y. Asahara, S. Nakayama & Y. Yoneda, "Gradient-Index Rod Lens Made by a Double Ion-Exchange Process", *Appl. Opt.* 27, 496-499 (1988)
2. S. N. Houde-Walter & B. L. McIntyre, "Dependence of Refractive Index on Silver Concentration in Gradient-Index Glass", *J. Non-Cryst. Solids*, 107, 316-322 (1989)
3. I. Fainaro, M. Ish Shalom, M. Ron & S. Lipson, "Interdiffusion of Silver in Glasses and the Related Variations in electronic Polarisability", *Phys. Chem. Glasses* 25, 16-21 (1984)
4. P. Chludzinski, R. V. Ramaswamy & T. J. Anderson, "Ion Exchange between Soda-lime-silica Glass and Sodium nitrate - Silver nitrate molten Salts", *Phys. Chem. Glasses* 28, 169-173 (1987)
5. A. K. Sbouh, D. E. Arafah & Y. Al-Ramadin, "Changes in the Composition of Soda-Lime Glass Resulting from Silver Doping", *Mat. Sci. & Eng. B3*, 473-477 (1989)
6. C. Kaps & W. Fliegel, "Sodium/Silver Ion Exchange between a Non-Bridging Oxygen-Free Boroaluminosilicate Glass and Nitrate melts", *Glastech. Ber.* 64,199-204 (1991)
7. J. E. Shelby & J. Vitko, Jr., "Colloidal Silver Formation at the Surface of Float Glass", *J. Non-Cryst. Solids* 50, 107-117 (1982)
8. P. Sarkar, J. Kumar & D. Chakravorty, "Microstructure and Optical Absorption of Silver Granules in Oxide Glasses Produced by Ion-Exchange and Reduction Treatments", *J. Mat. Sci. & Eng.* 18, 250-256 (1983)
9. F. Gervais, A. Blin, D. Massiot, J. P. Coutures, M. H. Chopinet & F. Naudin, "Infrared Reflectivity Spectroscopy of Silicate Glasses", *J. Non-Cryst. Solids* 89, 384-401 (1987)
10. V.V. Moiseev, "Ion Exchange and Constitution of Glass", *J. Non-Cryst. Solids* 42, 589-600 (1980)
11. B. Locardi & A. Lama, "A Thermodynamic Approach to Glass-Molten Salt Exchange Processes", *Phys. Chem. Glasses* 11, 71-74 (1970)