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Effects of silver and potassium ions on ion exchange in float glass

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The variation of optical and mechanical properties in ion-exchanged glasses was investigated. Ion exchange was carried out in KNO_3, $NaNO_3$ melts and their mixed melts with $AgNO_3$. The glasses used were soda–lime–silicate glasses produced by the float process. In order to analyse the effects of ion exchange, colour variation for optical properties, bending strength, surface microhardness and softening point for mechanical properties, and resistivity for electrical properties, were measured. In the optical properties, silver ions play an important role in colouring, ion exchange in the mixed melt of KNO_3 and $AgNO_3$, and additional heat treatment in air made it possible to obtain a range of colours from yellow to reddish–brown. Bending strength was increased by five times over the values of the parent glasses, surface microhardness was increased about 50 kg mm^{-2}, and the softening point was increased linearly with the amount of ion exchange resulting from ion exchange in the KNO_3 melt, because the potassium ion plays a great role in strengthening in the mechanical properties. On the other hand, in the mixed melt of KNO_3 and $AgNO_3$, bending strength and surface microhardness were increased slightly in contrast with the KNO_3 melt, and the softening point decreased on increasing the amount of ion exchange.

1. Introduction

Colouring of glass is classified as ionic colouring obtained by adding a colourant containing transition metal ions, and colloidal colouring obtained by adding platinum, gold, silver, copper and sulphide. In addition to these colourant additions to the batch, colloidal colouring due to ion exchange, by which it is possible to change the colour characteristics and also increase the strength at the same time, is well known.

In 1950, Rindone and Weyl carried out $Na^+ \rightleftharpoons Ag^+$ ion exchange of soda–lime glasses, and reported [1] that Ag^+ ions were reduced to Ag° atoms by Fe^{2+} and As^{3+} ions, and that the Ag° atom can aggregate and grow into particles of Ag° metal. As the result of studying the mutual relation between Ag^+ ions and multivalent ions such as As^{3+}, Sb^{3+} and Bi^{5+} ions, Kobayashi [2, 3] found that the optical absorption spectra of glasses containing colloid and multivalent silver ions show optical absorption at around 420 nm. Frischat [4] also reported ion exchange steps between a heavy metal ion of a melt and an alkali ion of a glass. Sakka and co-workers [5, 6] and Klonkowski *et al.* [7] reported that glasses containing Na_2O were coloured brown and strengthened at the same time when $Na^+ \rightleftharpoons Cu^+$ ion exchange was carried out in CuCl salt.

In this study, ion exchange treatment was carried out in KNO_3, $NaNO_3$ melts and their mixed melts with $AgNO_3$. We used 2 mm plate glasses produced by the float process for the parent glasses, and in order to analyse the effects of ion exchange, we measured optical characteristics, bending strength, surface microhardness, softening point, density and resistivity.

2. Experimental procedure

2.1. Ion exchange

The soda–lime–silicate glasses used were produced by the float process, which gave clear plate glasses of 2 mm thickness. The specimens were obtained by cutting the glasses into a suitable size for each measurement. Then they were polished with SiC papers, Al_2O_3 powder and diamond paste to remove microcracks at the cutting edge. They were then again washed with acetone and distilled water and then dried.

The salts used were KNO_3, $NaNO_3$ melts and their mixed melts with $AgNO_3$. The compositions of each melt are shown in Table I. The temperature of the ion-exchange treatment was varied from 430–480 °C for the KNO_3 melt because no strengthening effect can be

TABLE I Compositions of the melts used in this study

Salts	Compositions	Treatment temperature (°C)
KN	KNO_3 only	430–480
NN	$NaNO_3$ only	370–430
K2A	98 mol % $KNO_3 \cdot$ 2 mol % $AgNO_3$	370–430
K5A	95 mol % $KNO_3 \cdot$ 5 mol % $AgNO_3$	370–430
N2A	98 mol % $NaNO_3 \cdot$ 2 mol % $AgNO_3$	370–430

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expected to occur below 420 °C or stress relaxation to occur above 490 °C. For mixed melts with $AgNO_3$, the temperature was varied from 370–430 °C because of decomposition of $AgNO_3$. The duration of the ion-exchange treatment was varied from 0.5–24 h.

2.2. Property measurements

We analysed surface composition by electron diffraction spectroscopy (EDS) to measure the amount of diffused alkali or metal ions in the glasses and carried out line profile analysis to measure the ionic concentration distribution by using electron probe micro-analysis (EPMA) (JCXA-733, Jeol, Japan). Density changes were measured using a balance with a density determination kit, according to Archimedes' theory.

To obtain the optical characteristics, the glasses were cut into 35 mm × 35 mm × 2 mm pieces, and after ion exchange the spectral transmittance was measured using a UV–VIS spectrophotometer. According to ASTM E 308-85 (computing the colours of objects by using the CIE system), we calculated the colour-coordinates and excitation purity from the spectral transmittance.

To measure the bending strength, the glasses were cut into 250 mm × 40 mm × 2 mm pieces and ion exchange was carried out. The specimens were tested using an Instron (DCS-10 T, Shimadzu Co., Japan) under conditions of 100 kg load cell, 0.5 mm $\min^{-1}$ of crosshead speed and 130 mm loading span. From the tested values the bending strengths were calculated from

$$S = 3La/bd^2 \qquad (1)$$

where S is the bending strength, L is the fracture loading, a is half the loading span, b is the width and d is the thickness of the specimens.

Knoop hardness was measured with a 100 g load using a surface microhardness tester (Tukon, Page-Wilson Co., USA).

To measure the softening point, the glasses were cut into 25 mm × 4 mm × 2 mm pieces, and after ion exchange, they were measured using a Dilatometer (Motoyama PCR type, Shinko Electric Co., Japan).

Electric properties, were estimated by cutting the ion-exchanged glasses into 12 mm × 2 mm × 1.5 mm pieces and then polishing them. The cut edges were coated with silver paste (Emetron, Ag 75%), and 0.1 mm diameter copper wires were attached to specimens and the resistance was measured. From the measured resistance, the resistivity was calculated from

$$\rho = Rl/d \qquad (2)$$

where ρ is the resistivity, R is the measured resistance, l is the width and d is the length of the specimens.

3. Results

3.1. EDS analysis

The surface analysis spectra of ion-exchanged glasses are presented in Figs 1 and 2.

In the ion-exchange treatment in K2A shown in Fig. 1, elemental potassium and silver increase gradually and elemental sodium decreases with increasing ion-exchange treatment temperature.

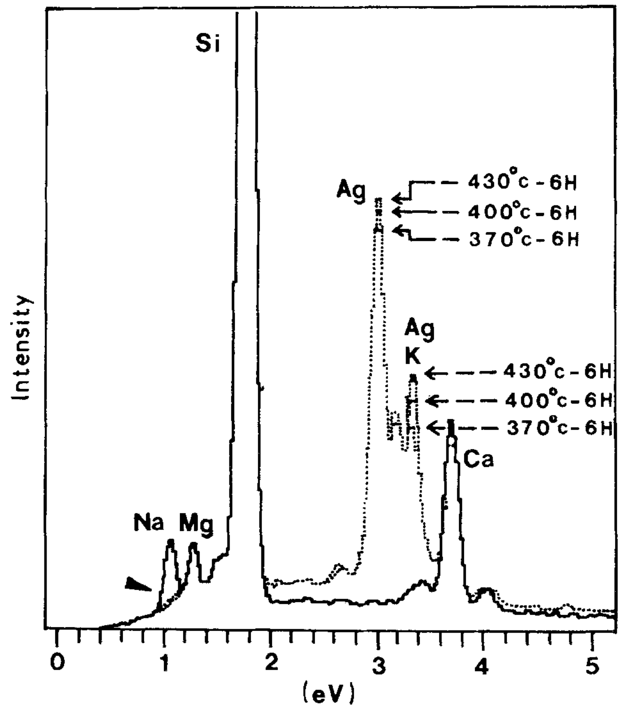

Figure 1 EDS analysis of ion-exchanged glasses treated in K2A. (——) Parent glass, (· · ·) ion-exchanged glass.

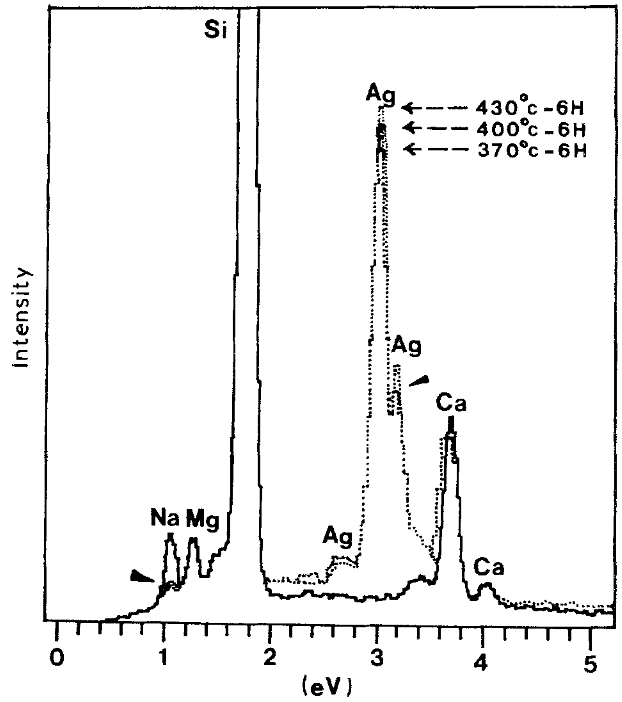

Figure 2 EDS analysis of ion-exchanged glasses treated in N2A. (——) parent glass, (· · ·) ion-exchanged glass.

In N2A shown in Fig. 2, the silver peak is more intensive than in K2A, because K^+ ions as well as Na^+ ions in the glasses were exchanged by silver ions in the melt.

The concentration profiles of the ion-exchanged glasses at 430 °C for 6 h in NN are presented in Fig. 3a, which shows the surface concentration change

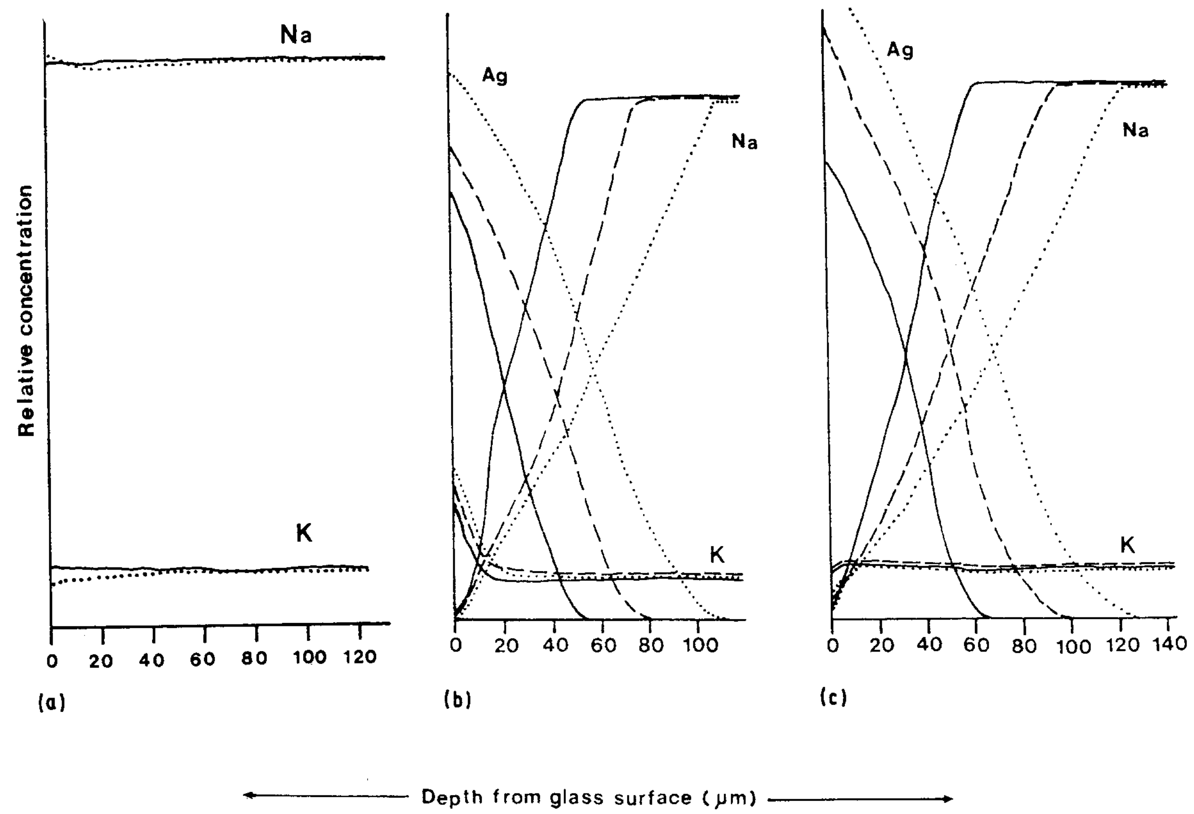

Figure 3 Concentration profiles of alkali and silver of ion-exchanged glasses (a) treated in NN, (b) treated in K2A, and (c) treated in N2A for 6 h. (a) (——) parent glass, (· · ·) 430 °C, 6 h; (b, c) (· · ·) 430 °C, (– – –) 400 °C, (——) 370 °C.

between Na^+ and K^+ by ion exchange. The concentration profiles after 6 h for K2A and N2A are shown in Fig. 3b and c, respectively. Elemental sodium decreases and while elemental silver and potassium increase with temperature, the diffusion depth of silver ions being deeper than that of potassium ions for K2A. Elemental sodium still exists at the surface for N2A.

3.2. Density

The density changes of the ion-exchanged glasses are shown in Fig. 4. Density increases with the amount of ion exchange for K2A and N2A.

A slight increase is shown in KN; if the annealing effect is considered, the increase due to ion exchange alone is about 0.001–0.002 g cm^{-3} in the experiments. There is little increase for NN, as for KN.

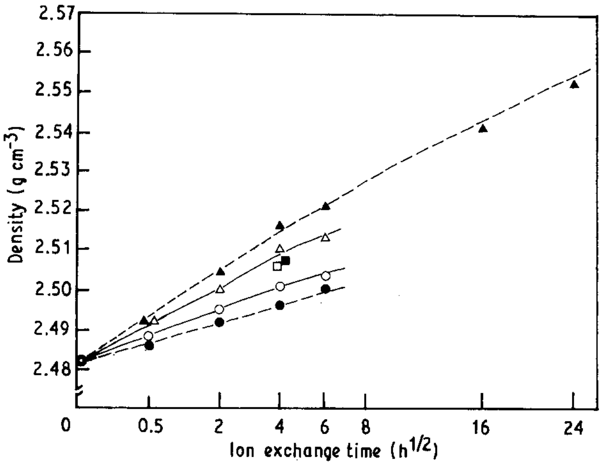

Figure 4 Density of ion-exchanged glasses, (△, □, ○) K2A and (▲, ■, ●) N2A, at (△, ▲) 430 °C, (□, ■) 400 °C, (○, ●) 370 °C.

3.3. Colour coordinates and excitation purity

The changes in colour coordinates from ion exchange and additional heat treatment in air are presented in Fig. 5a and b. Because the dominant wavelength treated in K2A is longer than that of N2A, the colour changes to almost red as shown in Fig. 5a. Fig. 5b shows that additional heat treatment in air produces a nearly pure colour, because of the increase in the amount of silver colloid. Colouring by ion exchange and additional heat treatment in air produced a dominant wavelength from 576.0–594.8 nm in this study.

The changes in excitation purity with ion exchange and additional heat treatment in air are shown in Fig. 6. The excitation purities were increased by ion-exchange treatment and the additional heat treatment in air produces a further increase. It can also be seen that the additional heat treatment induces growth of silver colloids, therefore colouring is further promoted.

3.4. Microstructure

Transmission electron micrographs of silver colloids in the ion-exchanged glasses treated in K2A and N2A are presented in Fig. 7a and b. The two cases are alike in the size of the silver particles colloid, 0.03–0.08 μm, but the particles are more abundant for N2A than for K2A. Fig. 7c shows a transmission electron micrograph of silver colloids in the reheated glasses after ion exchange in N2A. The additional heat treatment in air

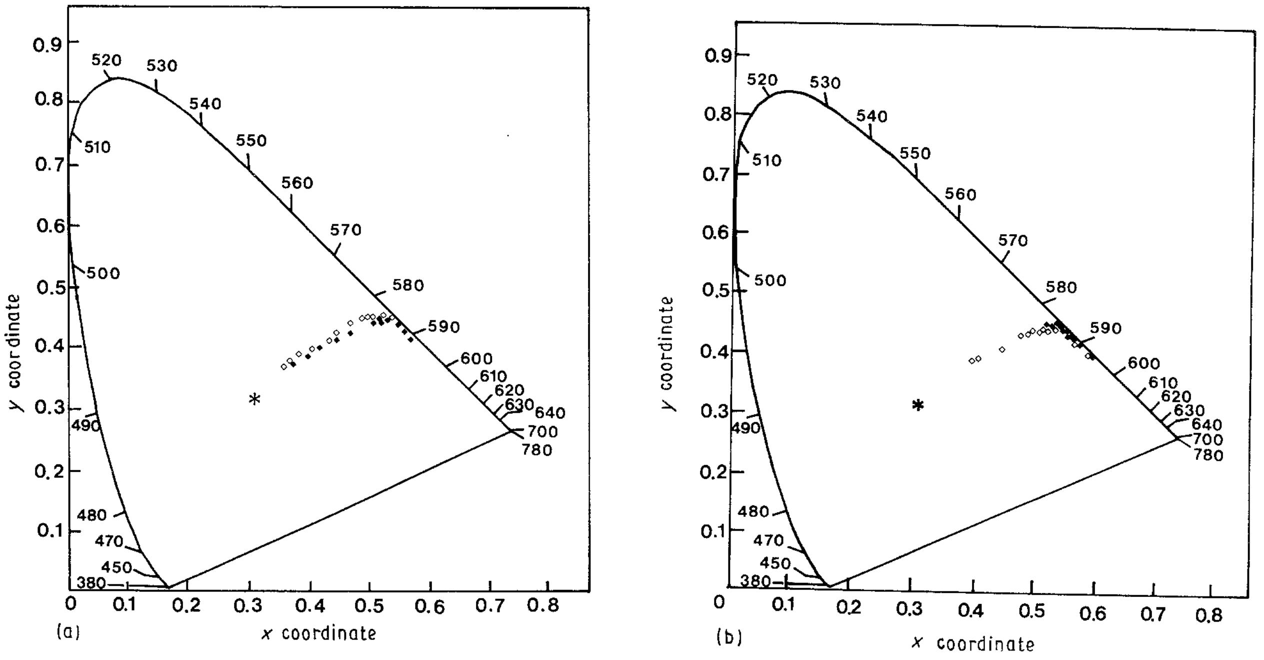

Figure 5 Chromaticity chart for (a) ion-exchanged glasses treated in (□) K2A and (■) N2A, and (b) (□) ion-exchanged glasses treated in N2A and (■) reheated glasses at 480 °C for 3 h. (*) Parent glass.

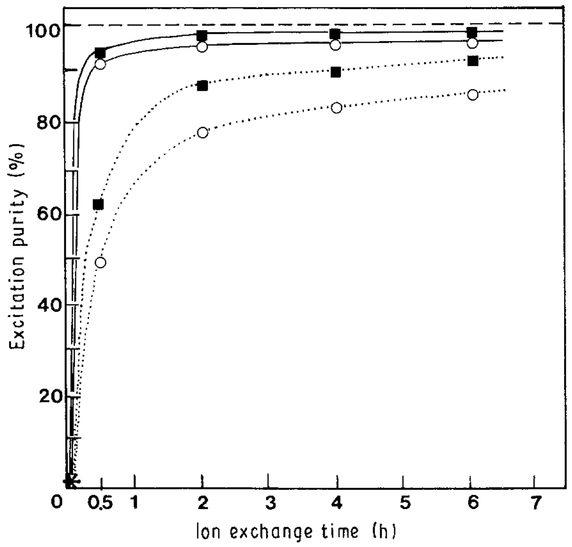

Figure 6 Excitation purity of ion-exchanged glasses treated in (○) K2A and (■) N2A at 400 °C. (*) Parent glass, (- - -) ion-exchanged glass, (——) reheated glass.

causes particle growth to about 0.1 μm. The shape of the silver colloids changes from spherical to needle shaped after additional heat treatment in air.

3.5. Bending strength

The effects of the amount of ion exchange on the bending strength are presented in Fig. 8. The bending strength of the parent glass is 10 kg mm^{-2} and is five times greater than that from ion-exchange treatment in KN. It increases 3–3.5 times after treatment in K2A and K5A, and 2.5–3 times after treatment in N2A. The present work shows that potassium ions play a greater role in strengthening than the silver ions.

3.6. Surface microhardness

The effects of the amount of ion exchange on the surface microhardness are presented in Fig. 9. The surface microhardness of the parent glass is

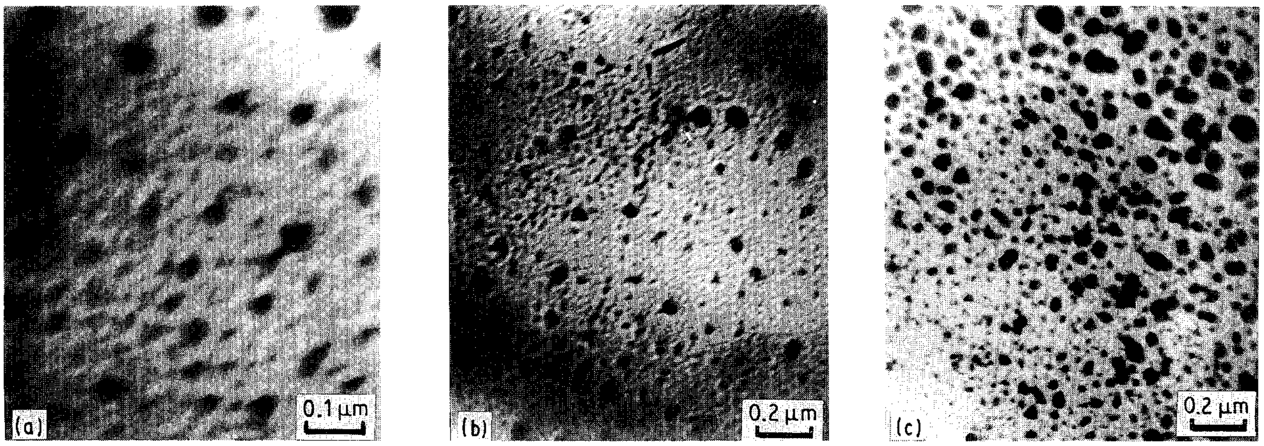

Figure 7 Transmission electron micrographs of silver colloids in ion-exchanged glasses (a) treated in K2A at 400 °C for 2 h, (b) treated in N2A at 400 °C for 2 h, and (c) as (b) reheated at 480 °C for 3 h.

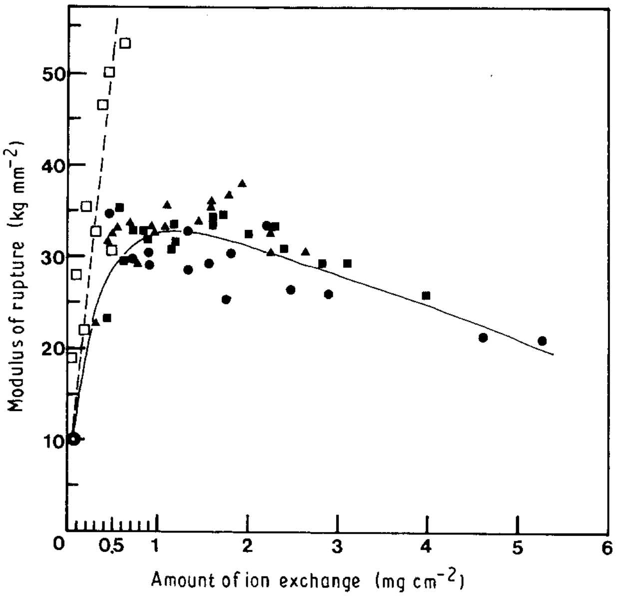

Figure 8 Bending strength of ion-exchanged glasses in (●) N2A, (▲) K2A, (■) K5A, (□) KN, (O) parent glass.

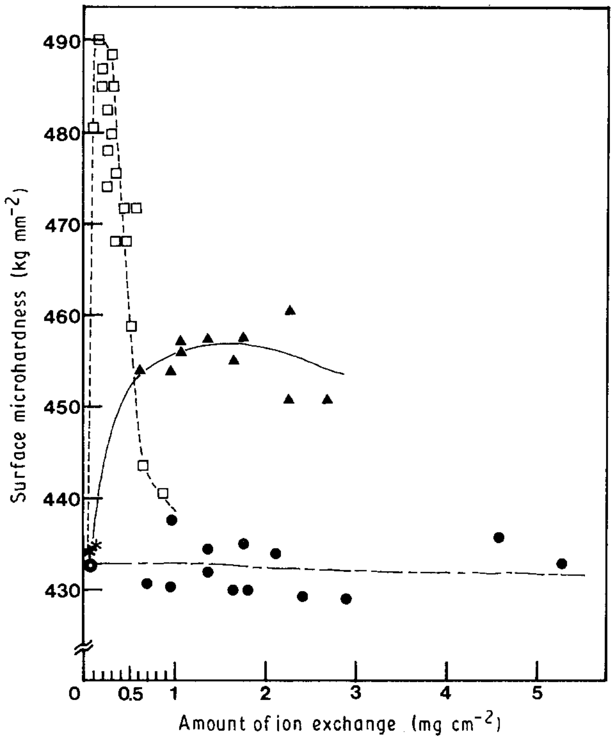

Figure 9 Surface microhardness of ion-exchanged glasses in (□) KN, (*) NN, (▲) K2A, (●) N2A, (O) parent glass.

433 kg mm^{-2} and this increases to 490 kg mm^{-2} after ion-exchange treatment in KN, and from 450 to 460 kg mm^{-2} after treatment in K2A. On the other hand, it shows little variation after treatment in N2A or NN.

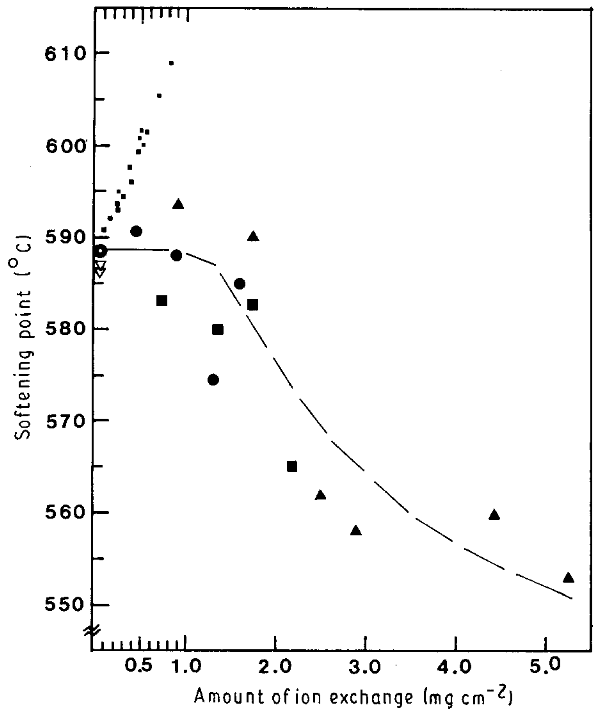

Figure 10 Softening point of ion-exchanged glasses in (■) KN; (▽) NN; (▲) N2A, 430 °C; (■) N2A, 400 °C; (●) N2A, 370 °C; (O) parent glass.

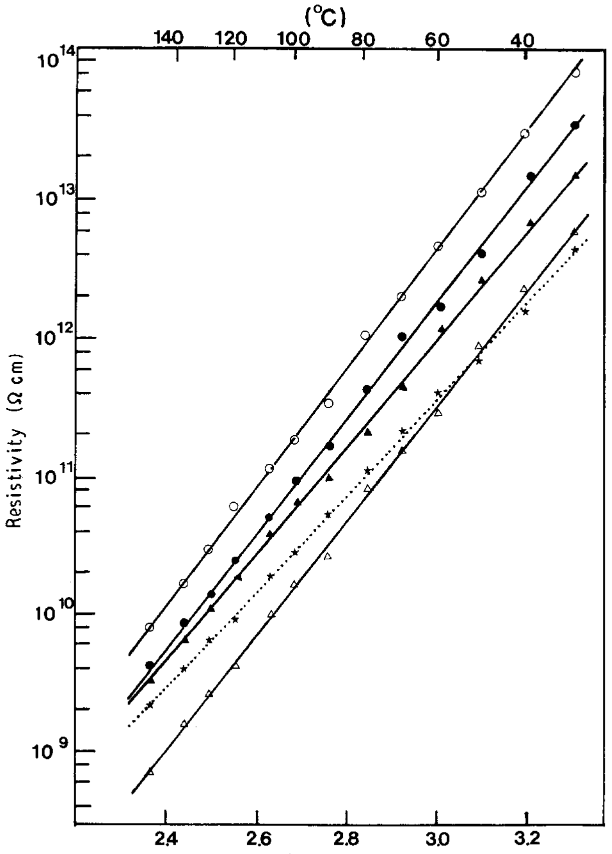

Figure 11 Resistivity of ion-exchanged glasses, in (○) KN, (●) K5A, (▲) N2A, (△) NN at 430 °C for 6 h; (---★---) parent glass.

3.7. Softening point

The effects of the amount of ion exchange on the softening points are presented in Fig. 10. We found that the softening points increased linearly with the amount of ion exchange, independent of the treatment temperature in KN. However, it shows somewhat lower values after treatment in NN, and decreased with the amount of ion-exchange treatment in N2A.

3.8. Resistivity

The changes in resistivity after ion exchange treatment are presented in Fig. 11. Resistivity decreased after treatment in NN from the parent glass values. But it increased in the other treatments such as KN, K5A and N2A. There is the highest increase for hand, it increased with respect to the parent glass for glasses treated in KN, and the lowest increase in N2A.

4. Discussion

It has been found that K^+ and Ag^+ ion-exchange treatment made it possible to colour as well as strengthen glasses. Potassium ion diffusion into glass did not produce colouring, but silver ions were reduced to Ag° metal by Fe^{2+}, Sn^{2+} ions and gave a colour range from yellow to reddish-brown. The additional heat treatment in air induces silver colloid growth and the colour changes from yellow to red. The size of the silver colloids was 0.02–0.1 μm; they were spherical in shape.

It can be seen that potassium ions play a more important role in improving the mechanical properties than silver ions. In glasses treated in KN, the bending strength was increased by five times above the parent glass value.

Treatment in K2A, K5A and N2A, when silver ions are the greater part of the ions diffused into the glass, increased the bending strength to three times of the initial value and then declined slowly. The surface microhardness was increased to about $40\,\mathrm{kg\,mm^{-2}}$ with treatment in KN, and 20–$25\,\mathrm{kg\,mm^{-2}}$ with treatment in K2A as a consequence of volume expansion of the glass surface region due to the variation in cation size [8]. Nevertheless, it decreased with the amount of ion exchange after treatment in N2A. There may be two reasons for this. The first, as shown in Figs 1–3, is that potassium ions in the glass diffused out into the melt and silver ions in the melt exchanged with potassium ions as well as sodium ions in glass, hence many more silver ions are diffused into glass. The second is that the silver ions are reduced to Ag° metal [2, 3]. Because the Knoop hardness is $530\,\mathrm{kg\,mm^{-2}}$ for soda–lime–silicate glass and $60\,\mathrm{kg\,mm^{-2}}$ for silver metal [9].

Density is mainly influenced by variation of weight, and the glasses treated in KN show a slightly lower increase; the density increased linearly with the amount of ion-exchange treatment in K2A and N2A because the diffusivity of the silver ion is 100 times higher than that of the potassium ion [10]. We also found that the softening points increased linearly with the amount of ion exchange, independent of the treatment temperature in KN. For Na^+ (glass) $\rightleftharpoons K^+$ (melt) ion exchange, the increase in softening point with the amount of ion exchange is linked to the bond strength of the network structure, i.e. viscosity variation: this increase agrees with the results of Shartsis *et al.* [11] and Boguslavskii and Pukhlik [12]. Shartsis *et al.* [11] reported that because potassium has a higher bond strength with non-bridging oxygens than sodium, K_2O shows a higher viscosity than Na_2O. Boguslavskii and Pukhlik [12] reported that substitution of K_2O for Na_2O causes an increase in the softening point. On the other hand, softening points are decreased with increasing silver ion contents, due to reduction of Ag^+ to silver colloid in the glasses. No electrostatic bond strength is found with the network structure, and thus viscosity is decreased.

The conduction of oxide glasses is quite dependent on alkali ions. In particular, soda–lime–silicate glasses show an ion conduction of sodium ions. That is, the conduction depends on the concentration and mobility of the sodium ions [13, 14]. Because the potassium ion has a lower mobility than the sodium ion, $K^+ \rightleftharpoons Na^+$ ion exchange causes an increase in resistivity. Glasses treated in KN show the highest increase. In glasses treated in NN, resistivity decreased due to the increase in sodium ion concentration.

5. Conclusions

Changes in properties of soda–lime–silicate glass induced by ion exchange were investigated. Ion exchange was carried out in KNO_3, $NaNO_3$ melts and their mixed melts with $AgNO_3$. Silver ions diffused into glasses reduced to Ag° colloid by Sn^{2+} mainly, and exhibited colours with a range from yellow to reddish-brown. The additional heat treatment in air induces growth of silver colloid, and therefore the colouring is further promoted. Bending strength increases five times after treatment in KN, and 2.5–3.5 times after treatment in K2A and N2A above the parent glass values. Surface microhardness increased on treatment in KN, but decreased as silver ions diffused into the glasses. The softening points are increased with potassium ion diffusion, but also decreased with silver ion concentration. Therefore, the present work shows that potassium ions play a greater role in improving mechanical properties than the silver ions. On the one hand resistivity is increased by substitution of potassium and silver ions for sodium ions on treatment in KN, K2A and N2A, but it is decreased by substitution of sodium ions for potassium ions after treatment in NN.

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