

PRECIPITATION OF AGCL CRYSTALS ON THE SURFACE OF ALUMINO-BOROSILICATE GLASS BY ION-EXCHANGE

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An alumino-borosilicate glass containing nano size AgCl particles was prepared by ion exchange process. The original melt-cast glass only contained Cl ions and silver ions were introduced to it through a post-ion exchange process. The line scanning analysis of cross sectioned areas, showed entering of Ag⁺ and K⁺ ions into the glass structure, and probably depletion of it from Li⁺ ions. Based on the Scanning Electron Microscopy results of the heat-treated glasses, it was deduced that this compositional modification encouraged liquid-liquid phase separation in ion-exchanged glasses and caused their opalescence occurring at a lower temperature as compared to the traditional method. Precipitation of nano-size AgCl crystalline particles during post-heat treatment of ion-exchanged glasses induced photochromism effect in them.

INTRODUCTION

Ion exchange in glass is a method by which some of the glass constituents can be exchanged with ions of a melt or solution in which the glass has been immersed. This method has been used extensively during last decades for the manufacturing of various optical devices like graded index lenses [1] which show flexibility and excellent repeatability of properties along with inexpensive raw materials and fabrication techniques [2-5]. Ion-exchange process has also been used for fabrication of photochromic glass [6-8]. In these experiments one or two steps ion-exchange process was followed by heat-treating of the resulted glass at nucleation and growth temperatures of silver halide [6-8]. An attempt was also made here to utilize this process for inducing photochromic effect in an alumino-borosilicate glass. Photochromic glasses are traditionally produced by casting of borosilicate glass melts containing photosensitive constituents. A high loss of silver salts occurring during melting of glass batches necessitates the introduction of new alternative methods, e.g. ion exchange, to reduce the processing temperature and the above-mentioned losses of constituent materials (2-4). At the present work the authors have tried to find i) the roles of ion-exchange process on the liquid-liquid phase separation of the glass and ii) the effect of the later phenomenon and also the crystallization of AgCl on the opalescence of ion-exchanged glasses during their post-heat treatments.

EXPERIMENTAL

Table 1 shows the silver-free, base composition of the photochromic glass, used in this experiment. It was derived by excluding 0.36 wt.% silver from a photochromic glass composition [9]. The raw materials were reagent grade chemicals, consisting of a high purity acid-washed silica (> 99.9 %), aluminum oxide (Merck, 5274840), lithium carbonate (Merck, 5671), potassium carbonate (Merck, 4924), P₂O₅ (Merck, 100540), Boric acid (Riedel-deHaen, 11606), CuO (Merck, 102761), potassium chloride (Merck, 4936), and potassium nitrate (Merck, 5061). The thoroughly mixed batches were melted in a platinum crucible in an electric furnace at 1450°C for 2 h and cast into a pre-heated cylindrical steel mold. The resulting glasses after annealing at 450°C (close to their dilatometric softening point) for 1 h, were cut, polished and lapped to form 30 × 10 × 1.8 mm slabs. The specimens then were immersed into a melt consisted of 4.7 wt.% silver nitrate and 95.3 wt.% potassium nitrate mixture at 400°C for differing ion exchange time periods of 2,4,6,8,10,12,14 and 16 h. Subsequently, they were washed in boiling distilled water to remove

Table 1. Chemical composition of glass.

Oxide	SiO ₂	Al ₂ O ₃	B ₂ O ₃	K ₂ O	Li ₂ O	P ₂ O ₅	Cl ⁻	CuO
wt.%	56.72	8.74	20.33	9.34	3.34	1.21	0.12	0.02

any contamination of salts. A two-step procedure was adopted for heat treatment of the resulting glasses. The specimens were at first heat treated at 400 for 30 min and subsequently treated at various temperatures in the 580 - 700°C range for 2 h. The temperature of 400°C was

considered as i) a temperature in which the silver ions can distributed more homogeneously in the ion-exchanged glass and ii) a nucleation step for AgCl crystallites. Within the interval 580-700°C, crystallization of AgCl proceeded. The crystallization of heat-treated glasses were investigated by X-Ray Diffractometry (Jeol, JDX-8030) and the diffusion profiles of Ag ions into the glass surface was investigated by the line scanning method (SEM, Philips, XL30 and Rontec Tescan, Vega II xmu).

Darkening was done via irradiation of the photochromic glasses by a 50W Osram lamp for 3 min, its peak wave-length of irradiation was 360 nm. A UV-VIS double-beam spectrophotometer (Vrio 2600 model, Chromophor, Germany) was used to measure the optical properties of the glasses.

RESULTS AND DISCUSSION

Figure 1 depict the diffusion profiles of silver ions and the microstructure of as received ion-exchanged glasses at different ion-exchange times. As it can be seen,

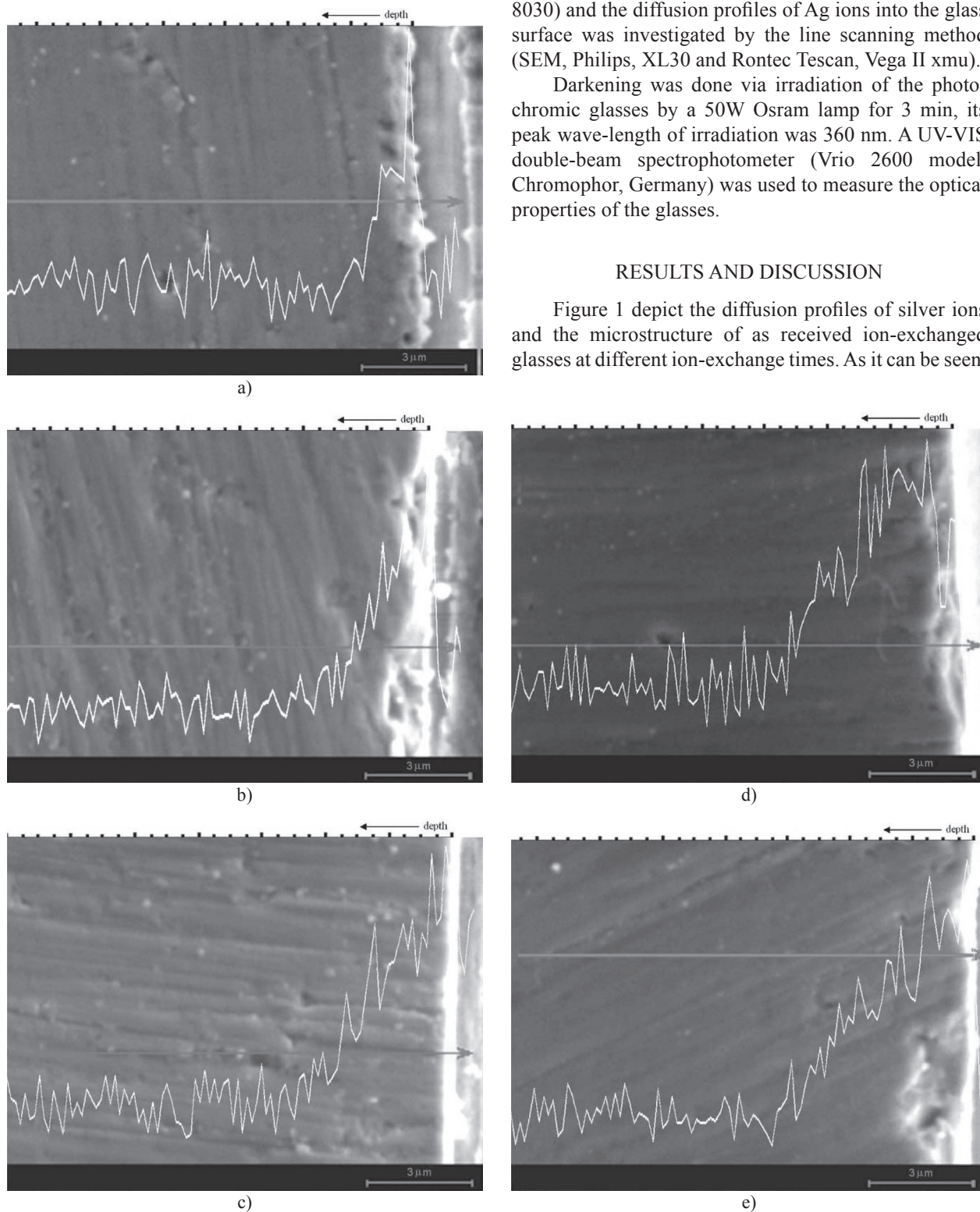


Figure 1. Diffusion profiles of silver ion and the microstructure of as received ion-exchanged glasses after a) 2, b) 6, c) 10, d) 14 and e) 16 h ion-exchange.

the diffusion depth of silver ion, relative to glass surface, increases from about 2.5 μm (Figure 1a) to about 6 μm (Figure 1e) with increasing the exchange time from 2 h to 16 h, respectively. In addition, the slope of diffusion profile was decreased with ion-exchange time, which indicated that while the concentration of silver ions at the glass surface remained almost constant, the diffusion depth was increased with time.

The electric charge of ion-exchanged glasses should remain balanced during the process. Therefore, considering the glass composition, it seems that silver ions from the melt should be exchanged with potassium / lithium ions or both from the glass. Figure 2 shows the distribution of potassium ion near the surface of a 10 h ion-exchanged glass. It indicates that the ion-exchange process has caused a little increase in the concentration of potassium. Therefore, it can be concluded that lithium has been substituted by silver ions during the process.

The presence of a concentration gradient of lithium between the glass and the molten bath and its small ionic radius makes the condition suitable for diffusion of lithium ions to the melt bath.

The results of the most heat-treated glasses showed that the above-mentioned ion exchange process has encouraged a liquid-liquid phase separation similar to those, which can be seen from comparison between Figures 3 and 4. These figures depict respectively the microstructures of an as received glass and a 16 h ion-exchanged specimen, after heat treatment at 600°C for 2 h. The comparison of the figures led to the conclusion that the modification of glass composition, i.e. entering of silver ions into the glass composition and reduction of its lithium content has made the glass more susceptible for liquid-liquid phase separation. In consistence with the fact that separation is a necessary phenomenon for precipitation of AgCl in the glass [5], the most ion-exchanged glasses showed the photochromic properties.

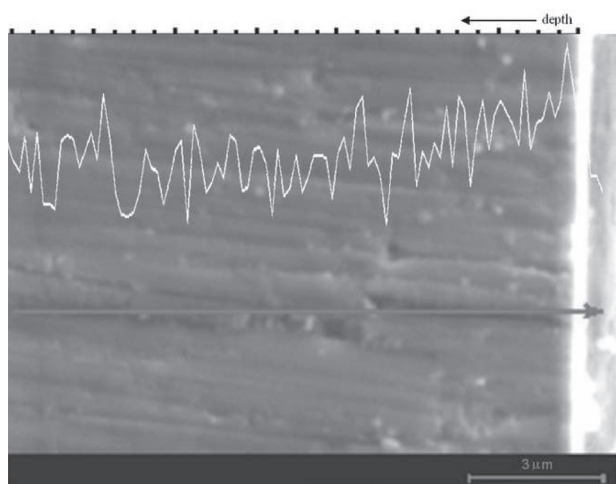


Figure 2. Diffusion profiles of potassium ion and the microstructure of as received ion-exchanged glasses after 16 h ion-exchange.

Figures 5 and 6 show the transmittance spectra of various ion-exchanged and heat-treated (at 600°C for 2 h) glasses versus wavelength, before and after irradiation by UV rays, respectively. The difference in transmittance of each series of glasses is clearer in the small visible wavelengths region. As it can be seen, in each series the absorption increases with longer ion exchange time and the absorption edge gradually shifts toward the long wavelengths. Entering of higher amounts of Ag ion with ion-exchange time and so precipitation of higher amounts of AgCl crystallites during heat-treatment of glasses should be responsible for gradual shifting of the absorption edge toward the longer wavelength, through light attenuation, viz. absorption plus scattering mechanism (5,10). Furthermore, the drop of transmission after irradiation by UV rays, especially between 460-554 nm, indicates the occurrence of darkening in the glasses. The results also show that darkening was increased with increasing the ion-exchange time, which can be attributed again to higher concentration of silver ions and consequently precipitation of more AgCl particles during heat-treatment. These crystalline particles introduce more metallic Ag clusters which are the entity that absorb visible light in much the same way

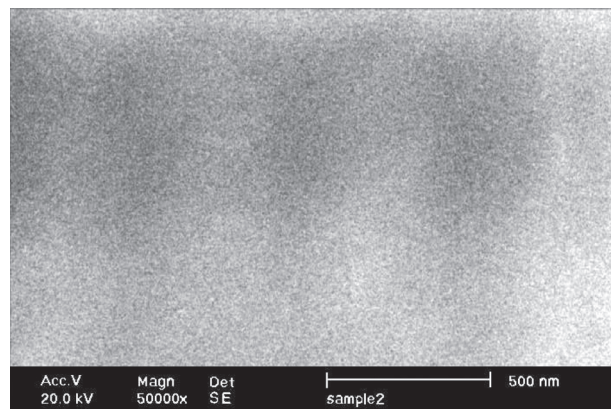


Figure 3. Microstructure of the glass, which merely had been heat-treated at 600°C for 2 h.

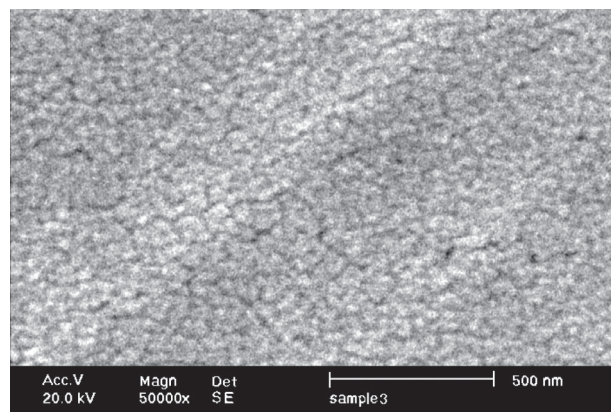


Figure 4. Microstructure of a heat-treated glass at 600°C that previously had been experienced ion exchange (for 16 h).

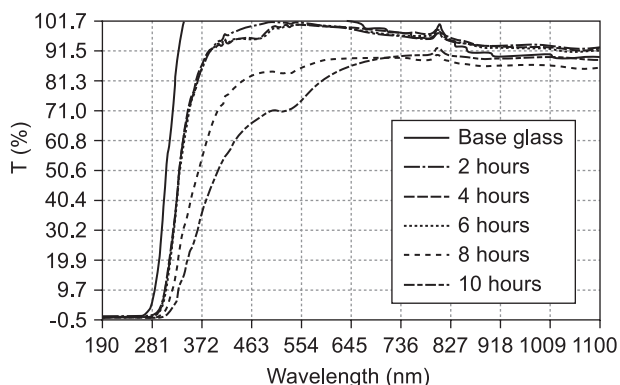


Figure 5. Transmission spectra of various ion-exchanged and heat-treated (at 600°C for 2 h) glasses versus wavelength, before irradiation by UV.

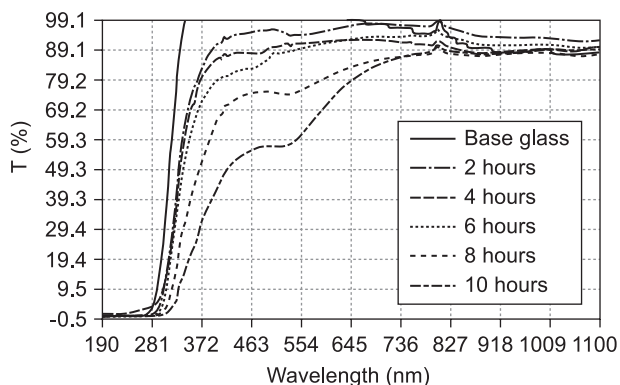


Figure 6. Transmission spectra of various ion-exchanged and heat-treated (at 600°C for 2 h) glasses versus wavelength, after irradiation by UV.

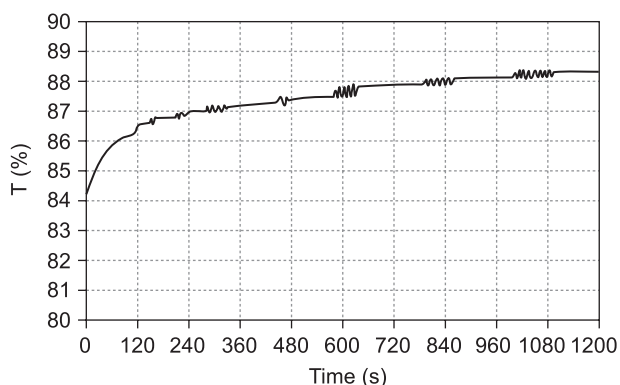


Figure 7. Fading rate of the photochromic glass obtained by heat-treatment of 6 h ion-exchanged glass at 600°C.

as does a metal and that causes the photochromic glass to appear dark. Regarding again the two figures clears that this later should be the main reason for absorption in the ion exchanged glasses at 460-554 nm.

Figure 7 depicts the fading rate of UV-irradiated glass (obtained through heat-treatment of a 6 h ion-exchanged glass at 600°C). The Figures 5, 6 and 7 point to the photochromic properties of the glass.

Figure 8 shows the X-ray diffraction patterns of the 16 h ion - exchanged glasses after heat-treatment at 560, 580 and 620°C, respectively. It can be seen that silver chloride precipitates above 560°C and its amount is considerably increased at 620°C. According to the Rayleigh equation, the maximum radius of AgCl crystallites in the alumino-borosilicate glasses should be kept less than 14 nm [5]. Otherwise, due to scattering of entered light by these particles, besides the occurrence of photochromism, the glasses would show the opalescence effects. The estimation of the mean diameter of precipitated AgCl crystals by Deby-Scherrer equation [11] utilizing the XRD patterns of crystallized specimens showed a crystalline radius of ~ 8.5 nm for the glass heat treated at 620°C. This radius is considerably smaller than the allowable radius, .i.e.14nm, which satisfies the transparency of glass. Therefore, it can be deduced that

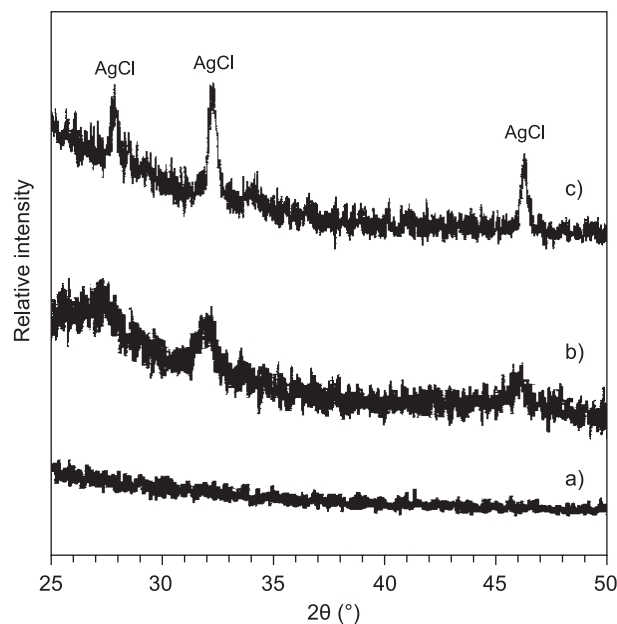


Figure 8. X-ray diffraction patterns of ion - exchanged (16 h) and heat-treated glasses respectively at a) 560, b) 580 and c) 620°C.

Table 2. Effect of ion-exchange time on the appearance of glass at various times and temperatures. Trans. means here transparent.

Ion exchange time (h)	2	4	6	8	10	12	14	16
Heat treatment temperature (°C)	600	620	600	600	600	580	600	560
Glass appearance	Trans	opal	Trans	Trans	Trans	Trans	opal	Trans

the opalescence of the glasses above 600°C should only be due to extension of liquid-liquid immiscibility.

The optimum heat treatment temperature of each glass was also determined as a function of ion exchange time. In each ion exchange experiment, this was the highest temperature at which the glass had the highest photo-sensitivity but least opalescence. These data were derived by analyzing the darkening rate vs. UV irradiation time curves and naked eye observation of heat-treated glasses, respectively. Table 2 represents the results of this experiment. As it can be seen, the optimum heat treatment temperature decreases from 600°C to 560°C for 2 and 16 h ion exchange times, respectively. As it was mentioned previously, the ion exchange process is associated with the enrichment of glass with silver ions and depletion of lithium ions. Therefore, it would be reasonable to assume that larger variations in composition taken place by the extension of ion exchange time have led to higher susceptibility to phase separation.

CONCLUSIONS

An alumino-borosilicate glass containing chlorine ions was exposed to an ion-exchange process. During this process lithium ions from the glass specimen were substituted by silver ions from the melt bath. Ion-exchange was time dependent and its development with time was led to reducing of temperature at which

the opalescence of glass occurred. Heat treatment of the ion-exchanged glasses led to precipitation of AgCl particles and appearance of photochromism in them. Our evaluation showed that the mean radius of the AgCl particles was about 8.5 nm.

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