



Non-conservation of the total alkali concentration in ion-exchanged glass



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ARTICLE INFO

Article history:

Received 12 November 2013

Received in revised form 22 December 2013

Available online 17 January 2014

Keywords:

Glass;

Ion exchange;

Chemical strengthening;

Alkali

ABSTRACT

Chemically strengthened glasses are widely used in applications requiring high scratch and damage resistance, such as cover glass for personal electronic devices. Chemical strengthening occurs by replacing the smaller alkali ions in the glass by larger alkali ions from a molten salt bath, whereby a surface layer with high compressive stress is installed. The mechanical properties of chemically strengthened glass strongly depend on the magnitude of the compressive stress, which in turn is proportional to the concentration of exchanged alkali ions. It has hitherto been assumed that the total amount of alkali ions in the glass is conserved during the ion exchange (e.g., in the Nernst–Planck model). In this work, we immerse alkali aluminosilicate glasses [30M₂O · 10Al₂O₃ · 60SiO₂ (mol%)] in MNO₃ salt baths containing identical alkali ions (where M = Li, Na, K). We demonstrate a non-conservation of the total amount of alkali ions in the glass during the ion exchange process. Generally we find that the smaller ions exhibit a net flux into the glass, while the larger ions demonstrate a net flux into the salt bath. Moreover, the total amount of alkali ions in the top surface layer is not conserved in sodium and potassium aluminosilicate glasses after ion exchange. We explain these findings based on the thermodynamic driving force difference in alkali oxides residing in glass or nitrate salt. The results are important for chemical strengthening applications, since the direction of flux and the non-conservation of alkali ions affect the final compressive stress of an ion exchanged glass.

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1. Introduction

Ion exchange has been used for more than a century for making tinted glass. Recently, the process has received renewed attention for applications in waveguide optics and chemically strengthened glass [1–4]. In the context of chemically strengthened glass, the ion exchange technique refers to a process in which an alkali-containing glass is immersed into a molten salt that contains a different alkali ion with larger ionic radius. In this process, the smaller alkali ions (generally Na⁺) residing in the glass surface are replaced by the larger ions in the molten salt (generally K⁺), which introduces a compressive stress in the surface of the glass. The stress profile can be expressed as

$$\sigma(x) = -\frac{BE}{1-\nu} (C(x) - \bar{C}), \quad (1)$$

where σ is stress, B is linear network dilation coefficient, E is Young's modulus, ν is Poisson's ratio, $C(x)$ is K₂O concentration at the depth x , and \bar{C} is the average K₂O concentration in the bulk of the glass [5–8]. This expression for compressive stress does not consider the effect of stress relaxation.

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Experimentally, numerous monovalent cations have been tested in ion exchange experiments, including the alkali ions (Li⁺, Na⁺, K⁺, Rb⁺, Cs⁺) as well as Cu⁺, Ag⁺, and others [9–13]. Corning® Gorilla® Glass [14,15] is a damage resistant glass that has been chemically strengthened by exchange of Na⁺ in the glass with K⁺ in the molten salt. Theoretically, it is typically assumed that the total amount of exchanged ions in the glass is replaced by the same amount of ions from the salt. This assumption has also been used to calculate the ion exchange kinetics via the Nernst–Planck equation and the resulting stress profile [9,16–18]. However, here we report the first comprehensive experiments showing that the total concentration of alkali ions is not conserved during the ion exchange process, and different alkali ions display qualitatively different behaviors.

2. Experimental procedure

Alkali aluminosilicate glasses containing only one type of alkali ion, namely Li⁺, Na⁺, or K⁺, were ion exchanged in molten alkali nitrate bath with the same type of alkali ions. The nominal compositions (in mol%) of the glasses were 30M₂O–10% Al₂O₃–60%SiO₂ (M = Li, Na or K). The utilized raw materials were SiO₂ (QP100 CGG sand, 99.99% purity), Al₂O₃ (alpha aluminum oxide, 99.9%), Li₂CO₃ (lithium carbonate, 99%), Na₂CO₃ (sodium carbonate, 99.78%), and K₂CO₃ (anhydrous potassium carbonate, 99.99%). To prepare the glasses, the batch materials were first thoroughly mixed for 60 min by ball mill. The

mixed batches were double melted in Pt crucibles in order to improve the chemical homogeneity. The first melts were heated at 1650 °C for 4 h and then roller quenched. The crushed pieces were re-melted at 1650 °C for 6 h and finally poured onto a stainless steel plate in air and then annealed for 1 h at 575 °C, followed by furnace cooling. The ion exchange experiments were performed on glasses cut and polished to final dimensions of $25 \times 25 \times 1 \text{ mm}^3$ where water was used as polishing medium. These specimens were submerged in the molten bath of certified grade alkali nitrate at temperatures and times described below. All samples were stored in a desiccator after sample preparation and salt treatment; however, there were some periods of time that samples were exposed to moisture. In order to analyze glass composition accurately, powdered sample was first dissolved in HF solution. The Al_2O_3 and SiO_2 concentrations were analyzed using inductively coupled plasma (ICP), and the major alkali cation concentrations were analyzed using flame emission spectroscopy (FES); the trace elements were analyzed using ICPMS.

The lithium-containing glass samples were ion exchanged in LiNO_3 at 300 °C (4 h), 370 °C (2 h, 4 h, 8 h, and 16 h), and 410 °C (2 h, 4 h, 8 h, and 16 h). The sodium-containing glass samples were ion exchanged in NaNO_3 at 370 °C (2 h, 4 h, 8 h, and 16 h) and 410 °C (2 h, 4 h, 8 h, and 16 h). The potassium-containing glass samples were ion exchanged in KNO_3 at 410 °C (4 h, 8 h, and 16 h) and 450 °C (2 h, 4 h, and 8 h). The ion exchange temperatures were chosen according to the respective glass transition temperatures and the mobility of the different alkali cations.

In order to study the conservation of alkali ions following the ion exchange process, depth profiling of the glass surfaces was performed using a magnetic sector SIMS (secondary ion mass spectroscopy) instrument (CAMECA IMS-4f). The experiments were conducted in negative mode, i.e., negative secondary ions were monitored. Generally, alkali elements are analyzed in positive SIMS mode, which provides better detection limit for these species than the negative mode. However, in our case, it is complicated to obtain depth profiles in glass substrates due to the high mobility of alkalis in the electric field originating from the non-compensated surface charge buildup generated by both the high energy primary ion beam and high energy electron beam for charge neutralization. In the negative mode, a cloud of low energy electrons is formed just above the sample surface and the positive surface charge arising as a result of ion bombardment is compensated by extracting the needed amount of electrons from the cloud. In this case, the regime of self-adjusted charge compensation is realized and the accurate depth profiles of alkalis can be obtained. The detection limit of alkalis in the negative mode is not as good as in the positive mode, but it has been shown that the application of an optimized charge neutralization technique allows for substantial increase in the used Cs^+ primary-ion current and, correspondingly, for improvement in the detection limit of Na up to $\sim 3 \times 10^{15} \text{ atoms/cm}^3$ [19].

In the present work, a 10 keV Cs^+ primary-ion beam with current density of $\sim 0.8 \text{ mA/cm}^2$ was rastered over an area of $\sim 100 \times 100 \mu\text{m}^2$. The base sample potential was -4.5 keV . The secondary ions were extracted over a $60 \mu\text{m}$ diameter optically gated area using a $750 \mu\text{m}$ field aperture and $150 \mu\text{m}$ image field. In order to resolve mass interference of the Na and K secondary-ion signals from the LiO and NaO signals, which are sufficiently intensive in the negative mode, a mass resolution of ~ 1900 was installed. The samples were coated with approximately 20 nm layer of gold. Sputtering rates were assumed to be constant and determined using crater depths measured by a Tencor P-10 stylus profilometer. The analyzed bulk concentrations from ICP and FES were used to calibrate the secondary ion mass spectrum (SIMS) to provide a quantitative comparison.

Besides the diffusion of alkali ions, it is believed that hydrogen/water also participates in the ion exchange process [20]. In a study of alkali leaching in sodium silicate and sodium aluminosilicate glasses, it was found that the H_2O diffusion in the glass controls the leaching of sodium ions bonded to non-bridging oxygens (NBOs), i.e., a sodium ion will be

Table 1

Glass chemistry determined by wet chemistry expressed in mol%, glass transition temperature by beam bending viscometry (where viscosity is equal to 10^{12} Pa s), room temperature density, and elastic moduli analyzed by resonant ultrasound spectroscopy.

mol%	LAS	NAS	KAS
Al_2O_3	9.93	9.80	9.98
SiO_2	61.80	59.70	61.11
Li_2O	28.24	0.0120	0.0002
Na_2O	0.0308	30.47	0.0105
K_2O	0.0007	0.0017	28.88
T_g (°C)	496	518	-
Density (g/cm^3)	2.394	2.503	-
Shear modulus (GPa)	34.8	26.7	20.8
Young's modulus (GPa)	85.6	66.9	52.4
Poisson's ratio	0.23	0.255	0.262

replaced by a hydrogen ion. In the case of sodium associated with tetrahedral aluminum groups in sodium aluminosilicate glasses, the sodium ions will be replaced by H_3O^+ [20]. Although in our work, Li^+ , Na^+ , K^+ -containing glasses were ion exchanged in molten nitrate bath with only the same type of alkali ion, water and other alkali ions appear as impurities in both glass and salt bath. Thus, the diffusion process involves majority cations but also the impurity cations. This is the reason we recorded all alkali ions including majority and impurity and also hydrogen in SIMS measurement.

3. Results and discussion

The analyzed compositions of the three base glasses are listed in Table 1. In both LAS (lithium aluminosilicate) and KAS (potassium aluminosilicate) glasses, Na_2O is the dominant impurity oxide with a concentration of about 100 ppm, while Li_2O is the dominant impurity oxide in NAS (sodium aluminosilicate) glass with a concentration of about 120 ppm. Water is also an impurity in all three alkali nitrate salts. The concentrations of the impurity cations in the salts are similar to those observed in the glasses (see Table 2).

The Li, Na, and K depth profiles of the treated LAS, NAS and KAS glasses did not show strong temperature or time dependence for the analyzed depth, which is about 6 to 10 μm . Thus, 16 h at 410 °C was chosen as a common condition to represent the depth profile of treated samples. The Li_2O depth profiles in the LAS glasses which have been ion exchanged in certified LiNO_3 bath for 16 h at 410 °C and in the base glass prior to treatment are shown in Fig. 1(a). The concentration values are plotted relative to the Li_2O concentration in the bulk. The base LAS glass has a constant Li_2O concentration from the outermost surface to the center, which is marked as reference in Fig. 1(a). Following the treatment in LiNO_3 bath, the lithium concentration in the top surface layer is higher than that in the bulk.

The Na_2O depth profiles in the NAS base glass and the ones which were ion exchanged in certified NaNO_3 bath for 16 h at 410 °C are shown in Fig. 1(b). Na_2O is depleted from the top surface layer of the base glass to a depth of about 300 nm, which corresponds to the hydration effect when hydrogen diffuses into the glass [20]. Following NaNO_3 treatment, the depth of the Na_2O depleted layer is preserved, but the

Table 2

Cation concentration in alkali nitrate salt analyzed using ICP-MS.

Salt (wt ppm)	Li	Na	K	Mg	Ca
LiNO_3	Major	15	2	<1	<1
NaNO_3	2	Major	N/A	35	12
KNO_3	<1	20	Major	<1	50
mol ppm	Li	Na	K	Mg	Ca
LiNO_3	Major	17	1.5	<1.7	<1.2
NaNO_3	5.3	Major	N/A	74	18
KNO_3	<3.4	33	Major	2.5	90

All values listed are in wt ppm. In addition, it is converted to mol ppm assuming alkali and alkaline earth are oxides and nitrogen as N_2O_5 .

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