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Effect of Al_2O_3 content on the mechanical and interdiffusional properties of ion-exchanged Na-aluminosilicate glasses

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ABSTRACT

The effect of the variation in the Al_2O_3 content on select physical properties of pristine and ion-exchanged glasses in the systems: $(75 - x)SiO_2$mol%-$25Na_2O$-xAl_2O_3 and $(75 - x)SiO_2$-$15Na_2O$-$10CaO$-xAl_2O_3, are reported. The surface compressive stress, surface hardness and K^+/Na^+ exchange ratio increase, while the depth of the inter-diffusion distance decreases, with increasing Al_2O_3 content. These trends are shown to be consistent with the compositional variation of the glass transition temperature and the molar volume, and their atomistic and thermodynamic bases are discussed.

1. Introduction

Chemical strengthening via ion exchange is commonly used in the industry to improve both the mechanical strength and the scratch resistance of glasses. The ion exchange process involves replacing smaller host alkali ions such as Na^+ in the glass with larger ions such as K^+, in a molten salt bath at a temperature below the glass transition temperature T_g. This process results in the formation of an ion-exchanged region near the glass surface that is under significant compressive stress, which tremendously improves the mechanical resistance of the glass [1,2].

Over the last decade, the increasing demand of highly damage resistant touch-screens has renewed the interest in the chemical strengthening process. However, the major drawback of this process is the high production cost due to the long timescale associated with the ion-exchange step. Nevertheless, a compromise between the production cost and the product quality can be struck by suitable adaptation of the bulk glass composition, which has led to the introduction of mechanically resistant commercial products such as the Asahi Dragontrail™, Corning Gorilla Glass™ and Schott Xensation™ [3]. All these products are based on alkali aluminosilicate glasses. It is well known that the alkali oxide: alumina ratio R is an important compositional parameter that controls the structure-properties relationship in these glasses. Therefore, an understanding of the effect of R on the ion-exchange process parameters will allow optimization of the mechanical properties of these glasses.

Previous studies in the literature primarily focused on the effect of R on self-diffusion of Na^+ in silicate glasses [4,5,6]. However, little is known regarding the effect of R on the Na^+-K^+ ion-exchange in alumino-silicate glasses with the exception of the study of Burggraaf and Cornelissen [7], which was based on a rather limited set of compositions and R values.

Na diffusion and Na^+-K^+ interdiffusions have been already studied in glasses with two network formers in the Na_2O-B_2O_3-SiO_2 glass system [8,9]. In $(Na_2O)_{0.2}$-$(B_2O_3)_y$-$(SiO_2)_{0.8-y}$ glasses and at constant temperature, the Na tracer diffusion coefficient decreases as the B_2O_3 content (y) increases [8]. According to Wu et al. [8], the change in the glass structure may be one explanation of this decrease.

In the present study, we report the results of a systematic investigation of the effect of R on the properties of ion-exchanged glasses in the systems $(75 - x)SiO_2$ mol%-$25Na_2O$-xAl_2O_3 $(0 \le x \le 25)$ and $(75 - x)SiO_2$-$15Na_2O$-$10CaO$-xAl_2O_3 $(5 \le x \le 15)$. In particular, this study focuses on the compositional dependence of the interdiffusional properties of Na^+ and K^+ and of the mechanical properties of the ion-exchanged glasses, such as the surface compressive stress and the surface hardness to establish the corresponding relationships between these properties and the atomic structure of these glasses.

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2. Experimental methods

2.1. Glass synthesis

The nominal glass compositions investigated in the present study are shown in Fig. 1. These glasses are characterized by different R = $[Na_2O]$ / $[Al_2O_3]$ or ($[Na_2O]$ + [CaO]) / $[Al_2O_3]$ ratios and were synthesized from constituent oxide and carbonate precursors: SiO_2 (Alpha products 99.5%), Al_2O_3 (Ceram Tm incorporated 99.5%), Na_2CO_3 (VWR 99.7%), $CaCO_3$ (Merck 99.5%). Approximately 300 g batches were melted in platinum/rhodium crucible between 1450 °C and 1650 °C for 2 h depending on the composition. The melt was then quenched and the resulting glass was crushed and remixed followed by remelting for two additional hours to facilitate homogenization. The final melts were subsequently quenched on a graphite plate and annealed for 12 h at the respective T_g, in order to release the internal stresses. The resulting glass compositions were analyzed by inductively coupled plasma mass spectrometry (ICP OES, Varian Vista MPX). The analyzed compositions are observed to be within ±1 mol% of the target compositions (see Table 1 and Fig. 1).

2.2. Density measurements

The densities of the glasses were determined at ambient temperature using the Archimedes' method with ethanol as the immersion medium. Reported densities are averages of three consecutive measurements on 3–5 g samples and are determined to within ±0.02 g/cm^3. The free molar volume was evaluated by the difference between the corresponding molar volume of the glass and the minimum theoretical volume occupied by the ions (ionic volume) [10]. Shannon's ionic radii were used to calculate the ionic volume [11]. The coordination number of Na was assumed to be 6, 2 for O and 4 for Al and Si.

2.3. Thermal analysis

Thermal analysis (DTA, Netzch STA 409 PC) was carried out to determine the glass transition temperature. Measurements were performed under helium atmosphere on 40–50 mg of glass powder taken in alumina crucibles. The T_g was determined to within ±2 °C, as the inflection of the glass transition region, using a heating rate of 25 °C/min.

2.4. Young's and shear modulus measurements

The Young's modulus and the shear modulus of the Na-aluminosilicate pristine glasses were determined using the impulse excitation technique (IET, IMCE RFDA professional). Rectangular samples with constant thickness (4.1 mm) and widths and lengths varying between 12 and 15 mm and 36 and 38 mm, respectively, were used. The IET technique consists in measuring the resonant frequency and the damping or internal friction of the glass samples [12].

The Young's and shear moduli are calculated using the relation [12]:

$$E = 0.9465\frac{m f_f^2 l^3}{wt^3}T$$

$$G = \frac{4lm f_t^2}{wt}\frac{B}{1+A}$$

where E and G are Young's modulus and shear modulus, respectively, m is the mass, l is the length of the sample, w = width, t is the thickness, f_f and f_t are, respectively, the flexural and torsion frequencies and T, A, B are all correction coefficients as defined in [12]. The measurements were performed at room temperature and the moduli were determined to within ±0.7 GPa.

Table 1
Nominal compositions (mol%) and non-bridging oxygen per Si + Al atoms (NBO/T) for all glasses synthesized in this study.

Glass	SiO_2	Na_2O	CaO	Al_2O_3	NBO/T
1	75	25		0	0.666
2	72	25		3	0.564
3	70	25		5	0.500
4	68	25		7	0.439
5	65	25		10	0.353
6	60	25		15	0.222
7	55	25		20	0.105
8	50	25		25	0.000
9	70	15	10	5	0.500
10	65	15	10	10	0.353
11	60	15	10	15	0.222

2.5. Surface hardness

The surface hardness of the pristine and the ion-exchanged glasses was measured by nanoindentation. Patterns consisting of 25 indents separated by 5 μm were recorded on the glass surfaces. The measurements were conducted with a Hysitron TriboIndentor equipped with a Berkovitch diamond tip. The load cycle consisted in loading from 0 to 3000 μN in 10 s, maintaining the load for 5 s before unloading over a period of 10 s. The surface hardness was calculated using the Olivier and Pharr method [13]:

$$H = \frac{P_{max}}{A}$$

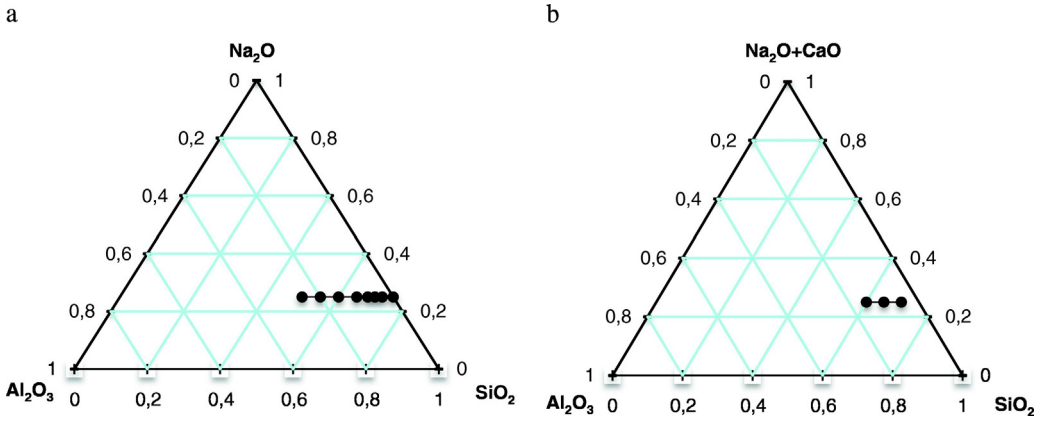

Fig. 1. Glass compositions (mol fraction) in the SiO_2-Na_2O-Al_2O_3 ternary system (a) and in the SiO_2-Na_2O-CaO-Al_2O_3 quaternary system (b), synthesized in the present study.