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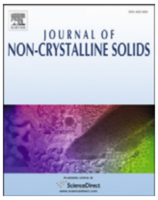

Sodium tracer diffusion in a sodium aluminosilicate glass

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ABSTRACT

Sodium tracer diffusion coefficients, D_{Na}^{*}, have been measured using the radioactive isotope Na-22 in a commercial, ion exchangeable sodium aluminosilicate glass at different temperatures between about 200 and 400 °C. The activation enthalpy derived from sodium tracer diffusion data for the as-received glass samples was found to be about 75.5 ± 1.2 kJ/mol and the value of the logarithm of pre-exponential factor of the sodium tracer diffusion coefficient, $\log_{10}\left[D_{Na}^{\circ}/(\mathrm{cm}^2/\mathrm{s})\right]$, is -2.58 ± 0.13. It was observed that pre-annealing the glass samples at the annealing point of 609 °C causes some reduction of the values of the sodium tracer diffusion coefficients. In addition, the glass samples investigated were found to take up water at 300 °C in wet air ($P_{H_2O} = 474$ mbar). However, an influence of the uptake of water during diffusion-annealing in wet air on the diffusivity of sodium was not observed.

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1. Introduction

The diffusion of sodium in a commercial, ion exchangeable sodium aluminosilicate glass, which is used as a parent glass for producing chemically strengthened glass by ion exchange, has been investigated in this study. Chemically strengthened glasses are widely used as protective covers for electronic displays, like laptop computer screens and mobile devices, as optical components and as high strength glass articles. Ion-exchanged alkali aluminosilicate thin sheet glasses have a high compressive stress and a deep compression layer near the surface. Such glasses, for example Corning® Gorilla® glass [1], have high resistance to scratch damage and high retained strength after use.

Chemical strengthening of glass by ion exchange was introduced in 1962 by Kistler [2] and Acloque and Tochon [3]. It is usually a process where glasses are immersed in a molten alkali salt bath at a temperature below the glass transition temperature, T_g. Provided that the ionic radius of the ions diffusing into the glass is larger than that of the ions which are simultaneously leaving the glass, glasses are strengthened during the thermally activated interdiffusion. The strengthening results in a high surface compressive stress that is created by inserting the penetrating larger alkali ion into sites occupied before by smaller host alkali ions and a lack of relaxation which would eliminate compressive stresses. Details of the chemical strengthening science and technology related to oxide glasses have been reviewed by several authors [4–11]. More complex chemical strengthening processes have also been discussed, for example, double and two-step ion exchanges. By re-introducing some of the initially replaced ions or by introducing another type of ion into the surface layer after a first ion exchange, the shape of residual stress profiles in glasses can be modified, potentially allowing to obtain strong glasses with low strength variability [12–14]. Compared to traditional thermal tempering, chemical strengthening generates a higher degree of surface compression without any significant optical distortion and can be applied to thinner glass products with complex geometry [6]. Chemically strengthened glasses exhibit higher impact resistance, scratching resistance, flexibility strength and resistance to temperature changes than glasses without chemical strengthening [8] and have a wide application in aircraft and high speed train windshields, bullet and blast resistant glasses, photocopier glasses, watch covers, and thin display glasses in electronic devices [7–9]. In 1964, Nordberg et al. [15] compared the strengths of four commercial glasses and two experimental glasses after identical ion exchange treatments and found that alkali aluminosilicate glasses were the best candidates for producing chemically strengthened glasses by ion exchange.

It is well known that the presence of water in glasses can affect their properties. Water in glass exists in two forms, as hydroxyl (OH) bonded to glass network formers and as molecular water dispersed in the interstices of the glass network [16]. Hydroxyl groups in oxide glasses are practically immobile while molecular water is mobile. Water molecules can be incorporated into glasses from surrounding, moisture-containing gas atmospheres by the reaction

$$\mathrm{H_2O\ (gas)} \rightleftarrows \mathrm{H_2O\ (glass)}. \tag{1}$$

Hydroxyl groups form when a water molecule diffusing within the glass encounters an energetically favorable oxygen bridge site through a reaction as that described in Eq. (2) [17].

$$\mathrm{R{-}O{-}R' + H_2O\,(glass)} \rightleftarrows \mathrm{R{-}O{-}H + H{-}O{-}R'} \tag{2}$$

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In Eq. (2) R and R′ denote parts of the glass network. This reaction may cause in oxide glasses a water-assisted structural relaxation and sometimes, associated with this, glass property changes, especially changes of some structure-sensitive properties like the glass transition temperature, T_g, the viscosity, the density, the refractive index, the dielectric constant of glasses [16] and the diffusivity of sodium in silicate glasses [18].

The work described in this article has two main goals. One goal is to determine experimentally the temperature dependence of tracer diffusion coefficients for the diffusion of sodium in the considered sodium aluminosilicate glass. The second goal is to examine whether the sodium aluminosilicate glass of interest in this study takes up water in a directly measurable amount upon annealing in moist air at elevated temperatures and also whether the uptake of water during diffusion-annealing in wet air influences the diffusivity of radioactive sodium in such a glass.

2. Experiments

The following sections provide details of the glass samples used in this study, how some information related to their composition was obtained, how their original water content was determined, how the uptake of water by such glasses was investigated and how the sodium tracer diffusion experiments were performed.

2.1. Glass samples

As received, the sodium aluminosilicate glass specimens (Corning Code 2317, obtained from Corning Inc.) were in the form of square plates with dimensions of 25 × 25 × 0.9 mm with both large sides well polished. Each specimen was usually cut into nine squares to have a sufficiently large number of samples available for experiments. To avoid any contamination by alkali and alkaline-earth compounds introduced by fingerprints, all glass samples were washed ultrasonically in de-ionized water, acetone and ethanol and tweezers were used thereafter to handle the glass samples for tracer diffusion and water content measurements.

2.2. Glass composition

Some information related to the chemical composition of the sodium aluminosilicate glass was obtained by X-ray photoelectron spectroscopy (XPS) and using a Surface Science Instruments (SSI) spectrometer Model SSX-100 which utilizes monochromated aluminum K-alpha X-rays with an energy of 1487 eV. The compositions of the original large surface and of a new cross-section surface created by breaking a glass sample in the middle were both determined in order to avoid any influence of contaminants possibly introduced during polishing.

2.3. Water uptake measurements

According to the literature, when the concentration of water is relatively small, almost all water in silicate glasses is accommodated in the form of OH groups [16]. A Bruker Optics Equinox 55 Fourier Transform Infrared (FTIR) Spectrometer was used in this study to determine the water content of glass samples by measuring the IR absorbance related to the presence of hydroxyl groups at wavenumbers between 3500 and 3700 cm^{-1}. To minimize the adsorption of water on glass surfaces, glass samples were ultrasonically washed with de-ionized water, ethanol, acetone, then dipped in HPLC grade acetone and after that dried in an oven at 130 °C for 10 min before determining data for the water content. 64 accumulated scans were performed over a wavelength range corresponding to wavenumbers between 400 and 4000 cm^{-1} to measure infrared spectra by using a KBr beam splitter and a deuterated triglycine sulfate (DTGS) detector. The three spectra with the lowest noise levels were selected for each sample for further data analysis.

The average concentration of water in the area of a glass sample through which the IR beam travels can be obtained from IR absorption measurements and using the Beer–Lambert law for data evaluation, Eq. (3) was used for this purpose.

$$C_{H_2O}=\frac{1}{2}\cdot\frac{A_g}{\varepsilon_{OH}\cdot d_g}\cdot\frac{M_{H_2O}}{\rho_g} = \frac{A_g}{\varepsilon_{H_2O}\cdot d_g}\cdot\frac{M_{H_2O}}{\rho_g} \tag{3}$$

with

$$A_g = -\log_{10}\left(\frac{I}{I_0}\right), \tag{4}$$

where C_{H_2O} is the mass fraction of H_2O in the glass, A_g is the measured absorbance of the glass, M_{H_2O} is the molar mass of H_2O (= 18.02 g/mol), ε_{OH} is the molar absorption coefficient related to the overall concentration of R–OH groups present in the glass (in L/(mol_{OH}·cm)), d_g (in cm) is the thickness of the glass sample, ρ_g is the density of the glass (in g/cm^3) and I/I_0 is the ratio between the integral intensities of the transmitted and the initial IR signals. The molar absorption coefficient of R–OH groups is equal to one half of the molar absorption coefficient of the overall water present in the glass, i.e., $2\,\varepsilon_{OH}\approx\varepsilon_{H_2O}$; both coefficients correspond to the stretching of R–OH groups.

Since the value of the molar absorption coefficient ε_{OH} for the considered sodium aluminosilicate glass is not available, Eq. (3) was reorganized to avoid the problem of not knowing this value, leading to Eq. (5).

$$C_{H_2O}\cdot\varepsilon_{OH} = \frac{1}{2}\cdot\frac{A_g}{d_g}\cdot\frac{M_{H_2O}}{\rho_g}. \tag{5}$$

If ε_{OH} does not change with the variation of water concentration in a given glass, the water concentration variation is proportional to that of the product $C_{H_2O}\cdot\varepsilon_{OH}$.

For measuring the uptake of water by the sodium aluminosilicate glass, a piece of a glass sample was held upright in an alumina sample holder and was annealed in a tube furnace in wet air at 300 °C. The wet air with $P_{H_2O} = 474$ mbar was generated by bubbling common air through de-ionized water at 80 °C and was pumped into the furnace at a rate of 20 L/h. Overall water contents were determined using FTIR after the samples were removed from the furnace, washed using HPLC grade acetone, and dried in an oven at 130 °C for 10 min.

2.4. Sodium tracer diffusion experiments

2.4.1. Diffusion mathematics

The thin film solution of Fick's second law applies to the diffusion of a tracer applied in the form of a thin film to a sample surface and diffusing in a homogenous glass sample in which the tracer diffusion coefficient is constant. The concentration of a tracer i, $C_i(\xi, t)$, at a distance ξ from the surface after diffusion-annealing for the time, t, is described by Eq. (6) [19].

$$C_i(\xi, t) = \frac{Q_i}{\sqrt{\pi\cdot D_i^*\cdot t}}\cdot exp\left(-\frac{\xi^2}{4D_i^*\cdot t}\right) \tag{6}$$

where D_i^* is the tracer diffusion coefficient of the species i, i.e., in this study of the radioactive sodium tracer Na-22, and Q_i is the initial concentration of this tracer per unit area.

The absorption of the gamma-radiation from the decay of the radioactive isotope used in the sample is negligibly small and can be ignored for the data analysis due to the relatively small tracer penetration lengths considered and the small absorption coefficient of Na-22 in sodium silicate glasses. Therefore the normalized residual

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