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Sodium tracer diffusion in sodium boroaluminosilicate glasses

Xinwei Wu [a], Jeremy D. Moskowitz [a], John C. Mauro [b], Marcel Potuzak [b], Qiuju Zheng [b], Rüdiger Dieckmann [a,*]

[a] Department of Materials Science and Engineering, Cornell University, Bard Hall, Ithaca, NY, 14853-1501, USA
[b] Science and Technology Division, Corning Incorporated, Corning, NY 14831, USA

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ABSTRACT

Sodium tracer diffusion coefficients, D^*_{Na}, have been measured using the radioactive isotope Na-22 in sodium boroaluminosilicate (NBAS) glasses containing either a small amount of As_2O_3 or Fe_2O_3. The chemical compositions of the first type of glasses are given by the formula $[(Na_2O)_{0.71}(Fe_2O_3)_{0.05}(B_2O_3)_{0.24}]_{0.2}[(SiO_2)_x(Al_2O_3)_{1-x}]_{0.8}$ and those of the second type of glasses correspond to the formula $[(Na_2O)_{0.73}(B_2O_3)_{0.24}(As_2O_3)_{0.03}]_{0.18}[(SiO_2)_x(Al_2O_3)_{1-x}]_{0.82}$. Tracer diffusion measurements were performed at different temperatures between 198 and 350 °C. Pre-annealing of the glass samples at their glass transition temperatures in common air was found to lead to changes in the values of sodium tracer diffusion coefficients. For the NBAS glasses containing Fe_2O_3, after pre-annealing for 5 h, the activation enthalpy derived for the sodium tracer diffusion increases almost linearly from 57.5 to 71.3 kJ/mol with a decrease in the alumina content while the pre-exponential factor of the sodium tracer diffusion coefficient increases from $2.1 \cdot 10^{-4}$ to $5.3 \cdot 10^{-4}$ cm^2/s. For the iron-free NBAS glasses pre-annealed for 5 h, the activation enthalpy varies between 63.9 and 71.4 kJ/mol while the pre-exponential factor varies between $1.5 \cdot 10^{-4}$ and $1.2 \cdot 10^{-3}$ cm^2/s. In addition, it was observed that the considered glasses take up water when annealed at 300 °C in wet air with $P_{H_2O} = 474$ mbar.

1. Introduction

Multi-component boroaluminosilicate glasses are widely used in various applications such as fiber glass in strengthened composites [1], substrate glasses in active matrix liquid crystal displays [2,3], high-level nuclear waste glasses [4–6] and as glass seals [7] due to their high chemical durability and mechanical strength [8]. Ion-exchanged alkali boroaluminosilicate glasses having high resistance to scratch damage are applied as protective covers for electronic displays in laptop computer screens and mobile devices.

In 1962, Kistler [9] and Acloque and Tochon [10] introduced chemical strengthening of glass through ion exchange. Glass samples are immersed in a molten alkali salt bath at a temperature below the glass transition temperature, T_g, during the ion exchange process. When the ionic radius of the invading ions like K^+ is larger than the ionic radius of the ions originally present in the glass samples such as Na^+, high surface compressive stress is generated through the thermally activated interdiffusion process and glasses are strengthened. The well developed chemical strengthening science and technology of glass has been reviewed by several authors [11–19]. Studying sodium tracer diffusion in alkali boroaluminosilicate glasses is important for better understanding ion diffusion in such glasses.

Sodium cations can play different roles in sodium boroaluminosilicate (NBAS) glasses. They can act as charge compensators for tetrahedral aluminum and/or boron and can form non-bridging oxygen (NBO) bonded to tetrahedral silicon and/or trigonal boron. To study how sodium tracer diffusion coefficients change with the structural roles that sodium ions play in the NBAS glasses considered in this article, the molar concentration ratio $[SiO_2]/[Al_2O_3]$ was varied while the concentrations of all other oxides were kept constant.

Water being present or incorporated into oxide glasses can cause a water-assisted structural relaxation via reactions such as that denoted in Eq. (1) [20]. This relaxation often leads to changes of structure-sensitive glass properties such as the viscosity, the glass transition temperature, T_g, the density, the dielectric constant, and the refractive index of such glasses [21] and also of the diffusivity of sodium in silicate glasses [22].

$$R{-}O{-}R' + H_2O(\text{glass}) \rightleftarrows R{-}O{-}H + H{-}O{-}R'. \quad (1)$$

In Eq. (1) R and R′ denote parts of the glass network. Since water can affect the diffusivity of sodium, it was also of interest to examine whether the NBAS glasses considered in this article take up water in directly measurable amounts.

* Corresponding author. Tel.: +1 607 255 4315; fax: +1 607 255 2365.
E-mail address: dieck@ccmr.cornell.edu (R. Dieckmann).

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2. Experiments

The following sections provide details of the glass samples used in this study, how these glass samples were made, their compositions and their original water contents. Furthermore, information is given on the experiments performed to investigate the uptake of water and the sodium tracer diffusion.

2.1. Glass samples

The NBAS glass samples, produced at Corning Incorporated, were square plates received with dimensions of about 10×10×1 mm with both large sides well polished. The glasses were made by melting powder mixtures containing appropriate amounts of Na_2CO_3, H_3BO_3, Al_2O_3, SiO_2, Fe_2O_3 and As_2O_3 in a covered Pt crucible at different homogenization temperatures for 6 h in air. In the case of iron-free glasses, about 0.1 mol% As_2O_3 was added as fining agent. To ensure chemical homogeneity, after the melts were quenched in water, the glass shards were remelted for another 6 h at their homogenization temperatures and then the melted glass was poured in air onto stainless steel plates. After that, the glasses were annealed for 2 h at different temperatures between 450 and 560 °C, depending on the chemical composition of the glasses. The compositions of the prepared NBAS glasses were determined by using wet chemistry analyses and are reported in Table 1.

At Cornell University samples with the dimensions denoted above were cut into quarters by using a diamond pen to have more samples available for tracer diffusion experiments. To avoid any contamination introduced by fingerprints, like alkali and alkaline-earth compounds, all glass samples were washed ultrasonically in de-ionized (DI) water, ethanol and acetone and thereafter tweezers were used to handle the glass samples for all types of measurements performed. Some preliminary values for sodium tracer diffusion coefficients for as-received glasses diffusion-annealed at 301 °C were already reported in Ref. [23]. These data were compared in Ref. [23] with transport-related data from different types of experiments involving the transport of sodium ions but in which the kinetics are limited by other factors.

2.2. Water content and uptake measurements

Almost all water being present in silicate glasses is accommodated in the form of hydroxyl groups as long as the concentration of water is relatively small [21]. To determine the water content of glass samples, the IR absorbance related to the presence of hydroxyl groups at wavenumbers between 3500 and 3700 cm^{-1} was measured by using a Bruker Optics Equinox 55 Fourier Transform Infrared (FTIR) spectrometer. Details about the procedures used for measuring water concentrations in glasses can be found in Ref. [24].

By making use of the Beer–Lambert law, the average water concentration in an area of a glass sample through which the IR beam travels can be obtained. Eq. (2) was used to convert measured absorbances of the glass, A_g, into values for the average mass fraction of H_2O in the glass, c_{H_2O}.

$$c_{H_2O} = \frac{1}{2}\cdot\frac{A_g}{\varepsilon_{OH}\cdot d_g}\cdot\frac{M_{H_2O}}{\rho_g} = \frac{A_g}{\varepsilon_{H_2O}\cdot d_g}\cdot\frac{M_{H_2O}}{\rho_g} \quad (2)$$

with

$$A_g = -\log_{10}\left(\frac{I}{I_0}\right). \quad (3)$$

In these equations I/I_0 is the integral intensity ratio between the transmitted and the initial IR signal, ε_{OH} is the molar absorption coefficient related to the overall concentration of hydroxyl groups present in the glass (in $L/(mol_{OH}\cdot cm)$), d_g (in cm) is the thickness of the glass sample, M_{H_2O} is the molar mass of H_2O (= 18.02 g/mol) and ρ_g is the density of the glass (in g/cm^3). The molar absorption coefficient related to the stretching of hydroxyl groups is about one half of the molar absorption coefficient of the overall water present in the glass, i.e., $2\ \varepsilon_{OH} \approx \varepsilon_{H_2O}$.

Eq. (2) was reorganized to avoid the problem of not knowing the value of ε_{OH} for the NBAS glasses considered in this study, leading to Eq. (4),

$$c_{H_2O}\cdot\varepsilon_{OH} = \frac{1}{2}\cdot\frac{A_g}{d_g}\cdot\frac{M_{H_2O}}{\rho_g}. \quad (4)$$

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

To measure the water uptake by a NBAS glass, glass samples of the size of about 5×5 mm with thicknesses of about 0.2 mm, were held upright in a thin slot of an alumina sample holder and were annealed in moist air in a tube furnace at about 300 °C. These glass samples were used to determine the relationships between the overall uptake of water and the annealing time for samples with unchanged water contents within glass samples near their centers. Samples of the same type were also used to measure the solubility of water in glass samples and to follow the uptake of water as a function of the annealing time in order to determine values of effective chemical diffusion coefficients, $\tilde{D}_{eff}$. All glass samples were annealed in a furnace containing wet air for a sufficiently long time. The wet air was obtained by bubbling common air through DI water at 80 °C (P_{H_2O} = 474 mbar) and was pumped through the furnace at a rate of about 20 L/h. Overall water contents were determined using a Bruker Optics Equinox 55 FTIR spectrometer after the samples were taken out of the annealing furnace, washed using HPLC grade acetone, and dried for about 10 min in an oven at 130 °C.

2.3. Tracer diffusion experiments

2.3.1. Experimental details

Tracer diffusion coefficients for the radioactive isotope Na-22 diffusing in NBAS glass samples were obtained by measuring residual radioactivities as a function of the distance from the surface where a thin film of solution containing isotope Na-22 was initially applied. The energies of γ-radiation associated with the decay of Na-22 are 0.51 and 1.28 MeV [25]. The initial radioactivity of a sample, A(x = 0,t), and the residual radioactivities of this sample, A(x,t), after removing of material

Table 1
Chemical compositions determined using a wet chemistry analysis, densities obtained at room temperature by employing an Archimedes' principle-based technique using a METTLER Toledo balance with ethanol as the immersion liquid, glass transition temperatures, T_g, defined as the temperatures at which the equilibrium viscosity equals 10^{12} Pa·s, and fractions of boron in tetrahedral coordination (N_4) determined by ^{11}B MAS NMR spectroscopy of the iron-free and iron-containing NBAS glasses investigated. The denotations used for glasses without Fe_2O_3 contain an "n" at the end. All data listed in this table were determined at Corning Incorporated and will be reported in Ref. [27].

Glass	Chemical composition (mol%)						Density (g/cm^3)	T_g (°C)	N_4 (at%)
	Na_2O	B_2O_3	Al_2O_3	SiO_2	Fe_2O_3	As_2O_3			
Al 2.5n	14.4	4.7	2.0	78.8		0.1	2.40	549	90
Al 5n	13.6	4.2	4.0	78.1		0.1	2.42	564	87
Al 7.5n	13.0	4.3	5.7	76.9		0.1	2.42	578	77
Al 10n	12.3	4.3	7.5	75.9		0.1	2.43	598	68
Al 12.5n	13.1	4.4	10.4	72.0		0.1	2.40	614	39
Al 15n	13.5	4.6	12.7	69.2		0.1	2.38	626	17
Al 2.5	14.6	4.9	2.2	77.4	0.9		2.44	543	
Al 5	14.6	5.0	4.7	74.7	1		2.44	551	
Al 7.5	14.7	4.9	7.6	71.8	1		2.46	573	
Al 10	14.8	5.0	10.3	68.9	1		2.44	577	
Al 12.5	14.3	5.0	12.6	67.1	1		2.41	591	
Al 15	14.3	5.0	15.6	64.1	1		2.42	631	