



Alkali diffusivity in alkaline earth sodium boroaluminosilicate glasses



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ABSTRACT

Understanding the fundamentals of alkali diffusion in boroaluminosilicate glasses is of critical importance for advanced glass applications, where the alkali diffusivity should be either enhanced or reduced. Here, we investigate the sodium–potassium interdiffusivity in thirty-six alkaline earth sodium boroaluminosilicate glasses with varying Si/Al ratio and type of alkaline earth cation by ion exchange experiments. The alkali mobility is maximized when Na⁺ acts as a charge compensator to Al³⁺ or B³⁺ in the glass rather than as a creator of non-bridging oxygen. In the peralkaline regime, the larger alkaline earth cations significantly slow down the motion of alkali ions, while this effect is much smaller in the peraluminous regime. Generally, there is a larger effect of increasing temperature on diffusivity for the larger alkaline earth cations than for the smaller ones.

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1. Introduction

The transport properties of oxide glasses have been of primary interest of both the fundamental research as well as the industrial research which focuses on practical applications in different technologies [1,2]. Boroaluminosilicate glasses are particularly widely used in the industry, since the mixing of the three network former cations (Si⁴⁺, Al³⁺, B³⁺) allows for delicate tuning of the glass properties [3]. Understanding the composition dependence of alkali ion transport in boroaluminosilicate glasses is of critical importance not only for chemically strengthened ion exchanged glasses [4–14], but also for boroaluminosilicate glasses as substrates for LCD/LED displays [15,16] and photovoltaics [17,18]. In the substrate applications, the diffusivity of the alkali ions should be kept as low as possible to avoid interference with the devices grown on these substrates. Hence, it is important to understand the composition and temperature dependence of alkali diffusion in these glasses in order to compositionally design new glasses with either enhanced or reduced alkali diffusion depending on the application.

Understanding the alkali diffusion characteristics is also of fundamental interest, e.g., for improvement of alkali mobility models and structural understanding of glasses and glassy dynamics [19,20]. Such understanding requires that the influence of chemical composition on network structure is well understood [21]. In this work, we study the diffusion kinetics of the K⁺-for-Na⁺ interdiffusion process, which has previously been investigated for various sodium silicate [22], sodium borosilicate [22], sodium aluminosilicate [23], sodium alkaline earth silicate [24], and sodium boroaluminosilicate [5] glass systems. For example, it has been shown that in sodium boroaluminosilicate glasses,

sodium is more mobile when it acts as a charge compensator to stabilize network formers than when it acts as a creator of non-bridging oxygens on tetrahedrally-coordinated silicon and trigonal boron [5]. However, many industrial compositions also contain alkaline earth cations, which are competing with the sodium cations for the role as charge compensator of tetrahedral aluminum and boron groups. In this study, we cast light on the impacts of network former speciation and modifier field strength on the alkali diffusivity in alkaline earth sodium boroaluminosilicate glasses over a wide compositional regime.

2. Experimental

We prepared a total of thirty-six alkaline earth sodium boroaluminosilicate glasses with either magnesium, calcium, strontium, or barium (in mol%): (76 – x)SiO₂–xAl₂O₃–6B₂O₃–12Na₂O–6RO with x = 0, 3, 6, 9, 12, 15, 18, 21, and 24 for R = Mg, Ca, Sr, and Ba. We also included 0.15 mol% SnO₂ as fining agent in all compositions. The preparation has been described in detail elsewhere [25,26]. All glasses were annealed for 2 h at their respective annealing points followed by slow (1 K/min) cooling. The analyzed chemical compositions of the final glasses were found to be consistent with the nominal ones within ± 0.5 mol%.

Ion exchange experiments were conducted in order to obtain the effective interdiffusion coefficient $\bar{D}_{\text{Na-K}}$ between Na⁺ and K⁺. This was done by immersing polished 25 × 25 × 1 mm³ samples in a molten salt bath of technical grade KNO₃ at 370, 390, 410, 430, and 450 °C for 8 and 16 h. Consequently, the large alkali ions (K⁺) from the molten salt bath exchange with the smaller alkali ions (Na⁺) in the host glass. This process results in the formation of a surface compressive stress. The penetration depth of the potassium ions was measured using an FSM-6000 instrument (Frontier Semiconductor). The K⁺-for-Na⁺

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interdiffusion gives the glass surface a higher refractive index than the interior, i.e., the surface can act as a waveguide. This is utilized in the FSM instrument to measure the saturation depth of the refractive index profile, which corresponds to the diffusion depth of potassium [27]. A total of eight FSM measurements were performed on each sample (using four 90° rotations per face).

3. Results and discussion

In the classical description of mutual diffusivity during an interdiffusion process, the interdiffusion coefficient D_{Na-K} is given by the Nernst–Planck equation,

$$D_{Na-K} = \frac{D_{Na}D_K}{D_{Na}N_{Na} + D_KN_K}, \quad (1)$$

where N_i and D_i are the fractional concentration and self-diffusion coefficient of alkali ion i , respectively. This equation is only valid under the assumption of thermodynamic ideality, i.e., $\partial \ln a_i / \partial \ln c_i = 1$, where a_i and c_i are the thermodynamic activity and concentration of alkali ion i , respectively. It is necessary to define the interdiffusion coefficient since the larger potassium ions diffuse at a slower rate than the smaller sodium ions, i.e., D_{Na-K} is different from the sodium self-diffusion coefficient (unless $N_{Na} = 0$). Furthermore, D_{Na-K} varies with local composition, temperature, and time [28]. We therefore define an average or effective interdiffusion coefficient (\bar{D}_{Na-K}) as a constant for a given diffusion profile. \bar{D}_{Na-K} is calculated based on the potassium diffusion depth combined with the interdiffusion time and temperature. The optical measurements provide the diffusion depth of the potassium ions as a result of the K^+ -for- Na^+ interdiffusion process. This depth is calculated from the number of fringes and width of the fringe pattern based on the data of TM mode of light propagation. An example of an optical fringe pattern is shown in Fig. 1.

The determined composition dependence of \bar{D}_{Na-K} at 410 °C is illustrated in Fig. 2. The composition dependence at the other investigated temperatures is essentially the same, despite the differences in activation energy discussed below. The data in Fig. 2 are plotted against the value of $[Al_2O_3] - [Na_2O]$, i.e., the excess concentration of Al^{3+} not being charge-balanced in tetrahedral configuration by Na^+ . For any given value of $[Al_2O_3] - [Na_2O]$, the diffusivity increases with decreasing size of the alkaline earth cation. The presence of relatively immobile alkaline earth cation lowers the alkali diffusivity and this effect is larger as the size of the divalent cation increases. As Al_2O_3 is substituted for SiO_2 and the network connectivity increases, the diffusivity exhibits a maximum value. The position of this maximum varies with the type of

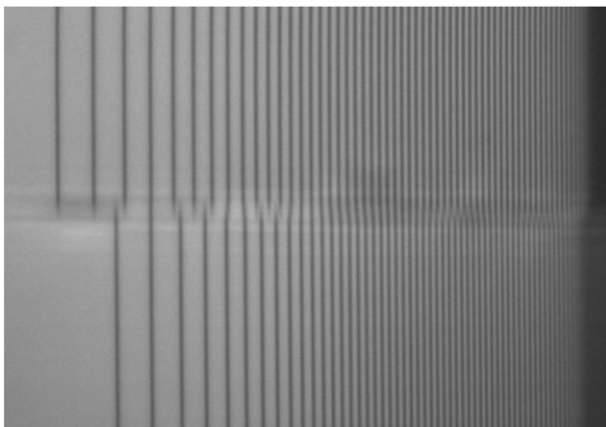


Fig. 1. Example of optical fringe pattern for a glass that has been immersed in molten KNO_3 . The upper set of fringes in the image corresponds to the TM mode of light propagation, while the lower set of fringes corresponds to the TE mode. The diffusion depth is calculated from the number of fringes and width of the fringe pattern based on the TM mode data.

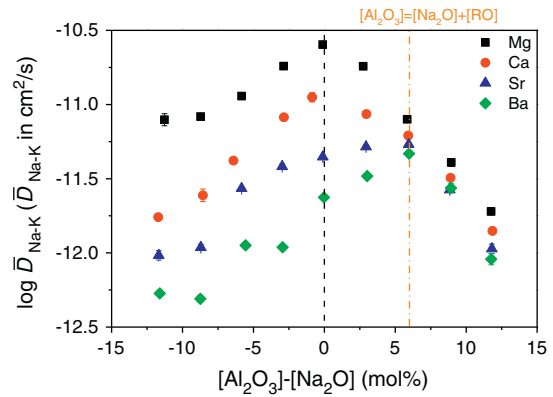


Fig. 2. Composition dependence of isothermal K^+ -for- Na^+ effective interdiffusion coefficient (\bar{D}_{Na-K}) as determined by interdiffusion experiments at 410 °C. The error bars of \bar{D}_{Na-K} correspond to the standard deviation of the eight measurements of the potassium diffusion depth for the same sample.

alkaline earth cation, as the maximum diffusivity is found at a higher Al_2O_3 content with increasing alkaline earth size (Fig. 2). We find that for the two glasses with the highest field strength cations (F), i.e., Mg^{2+} and Ca^{2+} , the maximum value of the interdiffusion coefficient is around the $[Al_2O_3] = [Na_2O]$ compositional point. The other two glasses with Sr^{2+} and Ba^{2+} , which have smaller field strength values, exhibit the maximum in interdiffusion coefficient at the composition corresponding to $[Al_2O_3] = [Na_2O] + [RO]$. For $[Al_2O_3] - [Na_2O] - [RO] > 0$, the effect of the type of alkaline earth cation on the alkali diffusivity is much smaller.

For the low- Al_2O_3 regime, some of the sodium ions are used to create non-bridging oxygens (NBOs) with Si–O or B–O. These sodium ions are found to be less mobile, e.g., Terai [29] reported that sodium diffusivity achieves its maximum value when AlO_4 tetrahedra are completely charge-balanced by Na^+ and no NBOs exist. This agrees with the results shown in Fig. 2 for the Mg- and Ca-containing glasses. For $[Al_2O_3] - [Na_2O] > 0$, the charge compensation of Al^{IV} must be performed by the divalent alkaline earth cations, which are not as effective for charge compensation as the monovalent sodium ions due to the difference in field strength [30]. This could explain the difference in the position of the maximum point in Fig. 2. These changes in glass network structure with composition are also reflected in the composition dependence of various physical properties [25,26]. For example, there is an approximate linear decrease of diffusivity with increasing refractive index independent of the type of alkaline earth cation (Fig. 3), since higher

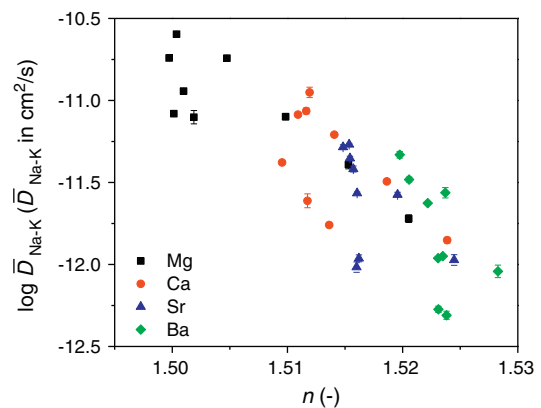


Fig. 3. Effective interdiffusion coefficient of K^+ -for- Na^+ (\bar{D}_{Na-K}) at 410 °C plotted as a function of the refractive index (n) at 589 nm of the sodium borosilicate glasses with magnesium, calcium, strontium, or barium. The uncertainty of n is ± 0.0003 . The values of n are taken from Ref. [26].

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