FULL PAPER

Effect of B₂O₃ substitution for SiO₂ in alkali aluminoborosilicate glasses on chemical strengthening

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This study reports the strengthening effect of partially substituting SiO₂ with B₂O₃ in aluminoborosilicate (ALBS) glasses. Specifically, it investigates how the B₂O₃ addition affects the ion-exchange behavior of the glass. The base composition of ALBS glass is 13Na₂O–5K₂O–7MgO–15Al₂O₃–12B₂O₃–48SiO₂ (mol %). In the prepared samples, the proportion of B₂O₃ was varied from 0 to 16 mol %. The Na⁺/K⁺ inter-diffusion coefficient of each sample was estimated from the K⁺ ion concentration profile collected along the cross-section of each sample after immersion in molten KNO₃ at ($T_g \times 0.83$) K (where T_g is the glass transition temperature) for 8 h. Adding only a small amount of B₂O₃ drastically changed the K⁺ ion concentration profile. In contrast, the activation energy of the Na⁺/K⁺ inter-diffusion was almost independent of B₂O₃ content. These results suggest that the B₂O₃ incorporated in the glasses simply acts as a flux component. These findings are useful for designing compositions that strengthen ion-exchanged glasses.

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1. Introduction

Chemically strengthened glasses are greatly demanded in the mobile device industry. Chemical strengthening, or ion-exchanging, is one of the most utilized techniques for improving the strength and safety of glasses.^{1)–4)} In ion-exchanged glasses, surface compressive stress (CS) is an important factor that controls the maximum strength of the glass. The other controlling factor is the depth of the ion-exchanged layer (DOL). A deeper DOL avoids cracking at the glass surface. Therefore, glass components with high CS and deep DOL values are required in the cover glasses of mobile devices.

Chemical strengthening is more or less accompanied by stress relaxation during ion-exchange at elevated temperatures.^{5),6)} For this reason, a high CS requires either a quick ion-exchange or a short immersion time in the molten KNO₃ bath. However, as ion-exchange is a diffusion process, extending the treatment time is a simple and effective method for increasing the DOL. Thus far, the high CS or deep DOL dilemma has been resolved by finding suitable components for chemical strengthening.

Ion exchanging behaviors are commonly investigated in soda-lime–silicate (SLS) glass. Although SLS glass is commercially available for various uses, increasing the DOL and enlarging the CS are not easily accomplished,

probably because non-bridging oxygens (NBOs) exist in this glass. The negative charge localized on the NBO impedes the movement of Na⁺/K⁺ ions during the ion-exchange.⁷⁾ For instance, when SLS glass is treated at 410°C for 8 h in a molten KNO₃ bath, the DOL is only 12 μm.⁸⁾ Such a shallow DOL cannot cover pre-existing cracks on the glass, which occur as general cracks at depths of the order of 1–10 μm. Some of these pre-existing cracks may be deeper.^{9)–13)} Under a tensile stress, a pre-existing surface crack concentrates the stress and degrades the strength of the glass. However, as mentioned above, prolonging the treatment to increase the DOL decreases the CS and hence the maximum strength.⁶⁾

Alkali aluminosilicate (ALS) is a superior glass composition for chemical strengthening. As is well known, the strength of sodium aluminosilicate glass is maximized at a molar ratio of Na₂O:Al₂O₃ = 1.0.¹⁴⁾ The sodium ions in this composition predominately act as charge compensators of the AlO₄[–] units, and are more easily moved than those bonding with NBOs.¹⁵⁾ After immersion at 410°C for 8 h in a molten KNO₃ bath, the DOL of ALS glass is 50 μm.⁸⁾ Although this result supports that ALS glass is among the best candidates for chemical strengthening, the high melting point of Al₂O₃ in the batch is limiting its maximum content in actual production because increasing the Al₂O₃ content in the glass batch increases the energy demands and cost of the glass production.

The melting temperature can be reduced by adding B₂O₃ as a flux component. The B₂O₃ lowers the temper-

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ature of the batch reactions, so the Al_2O_3 -containing glass batch can be melted without any capital expenditure such as special and expensive refractories that endure extremely high temperatures. It also reduces the emissions of carbon dioxide and other gases.

The major drawback of B_2O_3 addition is its seemingly negative effect on the ion-exchange. In an early review, Nordberg et al.¹⁶⁾ reported that borosilicate glasses are not strengthened by ion exchanging, and that borons in the glasses depress the ion-exchange rate. However, we have since reported a faster ion-exchange in aluminoborosilicate (ALBS) glass than in SLS glass, although the B_2O_3 contents exceeded 10 mol %.¹⁷⁾ How the composition affects the inter-diffusion coefficient of the Na^+/K^+ ion-exchange reaction in multicomponent ALBS glass, and the role of B_2O_3 in chemical strengthening, have been rarely reported. To elucidate these phenomena, the present study evaluates the effect of the B_2O_3 content in ALBS glass on the ion-exchange rate, and the role of the B_2O_3 component in the Na^+/K^+ ion-exchange mechanism.

2. Experimental procedures

The base glass composition in this study was $13\text{Na}_2\text{O}-5\text{K}_2\text{O}-7\text{MgO}-15\text{Al}_2\text{O}_3-12\text{B}_2\text{O}_3-48\text{SiO}_2$ (mol %), as reported in a previous study.^{8),17)} The B_2O_3 content of the glass was varied from 0 to 16 mol % in 2 mol % steps (see **Table 1**). The B_2O_3 component partially replaced the SiO_2 in the base glass composition. In Table 1, the number in the sample name denotes the molar content of B_2O_3 ; for

example, B12 denotes that the glass contains 12 mol % of B_2O_3 in the batch. Batches of 500-g glasses were prepared from reagent-grade powders of Na_2CO_3 , NaNO_3 , K_2CO_3 , KNO_3 , MgO , $\text{Na}_2\text{B}_4\text{O}_7$, $\text{Al}(\text{OH})_3$, and SiO_2 . The appropriately weighted powders were mixed thoroughly and roughly melted in clay crucibles at 1350–1500°C for 1.5 h in an electric furnace. The melted glasses were quenched in water at room temperature and dried. The roughly melted glasses were re-melted in a Pt–Au crucible at 1350°C for 4 h in an electric furnace. The re-melted glasses were heated to temperatures near their glass transition temperatures $[(T_g + 30)\text{K}]$, where T_g is the glass transition temperature, held for 30 min, and then cooled at 3 K/min to obtain annealed glasses. The T_g of each glass was measured by a thermomechanical analyzer (TMA, SII SS6000). All obtained samples were grounded, lapped with diamond slurry, and then polished with cerium oxide to obtain optically smooth surfaces. Their compositions were analyzed using a wavelength dispersive X-ray fluorescence spectrometer (Rigaku ZSX100e). Quantitative analysis was performed by a fundamental parameter method. The B_2O_3 content was accurately determined by the calibration curve method. Table 1 summarizes the analyzed compositions of each glass. Each value shown in Table 1 is the average of at least two measurements.

The physical and mechanical properties of the glasses are given in **Table 2**. The glass density was measured by Archimedes' method with distilled water as the immersion liquid. The number of oxygen atoms per volume (N_{O} , nm^{-3}) was determined from the density ρ and chemical composition of the glass.

The crack formation probability was measured before the ion-exchange process. The crack resistance must be measured before ion-exchange because it models the damages during the processing and handling before strengthening. The crack formation probability was determined on a Vickers hardness tester (Akashi MVK-H1). The indentation was made under a 1.96 N load in distilled water at room temperature. Consistent with a previous study,¹⁷⁾ a few drops of water were placed on the glass surface prior to indentation. The water environment was

Table 1. Chemical compositions of the glasses (mol %)

Name	Na_2O	K_2O	MgO	B_2O_3	Al_2O_3	SiO_2
B0	12.7	4.5	6.6	0.0	16.0	60.1
B2	12.8	4.5	6.6	2.1	16.0	57.9
B4	13.2	4.6	6.1	4.2	15.9	55.8
B6	13.2	4.6	6.0	6.1	15.9	54.0
B8	13.3	4.7	6.1	8.0	16.0	51.9
B10	13.3	4.6	6.1	9.9	15.9	50.0
B12	13.1	4.5	6.2	11.4	16.0	48.4
B14	13.3	4.4	6.1	13.3	16.1	46.6
B16	13.1	4.3	6.1	15.0	16.1	45.1
Experimental error	± 1	± 1	± 1	± 1	± 1	± 2

Table 2. Physical and mechanical properties of the glasses

Name	T_g (°C)	ρ Density (g/cm^3)	N_{O} Number of oxygen per volume (nm^{-3})	E Young's modulus (GPa)	ν Poisson's ratio	G Shear modulus (GPa)	K Bulk modulus (GPa)	Crack formation probability at 1.96 N in water (%)	H_v Vickers hardness (GPa)	$\bar{D}$ Inter-diffusion coefficient (cm^2/s)	DOL* (μm)	CS (MPa)
B0	691	2.47	42.2	75.8	0.221	31.0	45.3	0.0	5.68	2.01×10^{-09}	—	—
B2	654	2.46	42.5	74.2	0.224	30.3	44.8	4.0	5.64	4.31×10^{-10}	116(± 15)	820
B4	602	2.45	42.8	72.0	0.231	29.3	44.6	7.5	5.58	3.01×10^{-10}	69(± 10)	712
B6	580	2.45	43.0	70.3	0.232	28.5	43.7	3.8	5.46	1.55×10^{-10}	51(± 5)	734
B8	563	2.44	43.0	68.8	0.238	27.8	43.8	17.5	5.31	7.21×10^{-11}	46(± 4)	776
B10	569	2.43	43.2	67.6	0.241	27.2	43.5	62.5	5.23	9.51×10^{-11}	47(± 4)	757
B12	547	2.42	43.4	66.5	0.245	26.7	43.5	83.8	5.15	4.55×10^{-11}	37(± 3)	793
B14	545	2.41	43.5	65.2	0.247	26.2	42.9	80.0	5.09	5.05×10^{-11}	35(± 3)	733
B16	544	2.40	43.7	64.1	0.251	25.6	43.0	86.3	4.89	3.25×10^{-11}	31(± 3)	732
Experimental error	± 1	± 0.01	± 0.01	± 0.3	± 0.001	± 0.3	± 1	± 7	± 0.3			± 100

*Values in parentheses are uncertainties.

employed because it promotes cracking on glass with high crack resistance. The indentation duration was set to 10 s. The crack formation probability under a given indentation load was determined from 30 indentations on each glass, as reported in a previous paper.⁸⁾

The Vickers hardness H_v was measured at 0.29 N in air using the above-described hardness tester. The Young's modulus was determined by the pulse echo method using a DPR300 Pulser/Receiver (JSR Ultrasonics). The longitudinal and shear wave sound velocities (V_l and V_s , respectively) of the sample were measured using different transducers. Each velocity was determined from the sample thickness d and the round trip transmit time s , as follows:

$$V_l \text{ or } V_s = \frac{2d}{s}. \quad (1)$$

The Young's modulus (E) was calculated from the density ρ and the longitudinal and shear wave sound velocities:

$$E = V_s^2 \rho \frac{3V_l^2 - 4V_s^2}{V_l^2 - V_s^2}. \quad (2)$$

The shear modulus (G), Poisson's ratio (ν), and bulk modulus (K) were respectively calculated by the following equations:

$$G = \rho V_s^2, \quad (3)$$

$$\nu = \frac{1}{2} \frac{V_l^2 - 2V_s^2}{V_l^2 - V_s^2}, \quad (4)$$

$$K = \frac{E}{3(1 - 2\nu)}. \quad (5)$$

The glass samples were chemically strengthened by ion-exchange in KNO₃ molten salt at a treatment temperature of ($T_g \times 0.83$) K. The constant 0.83 was decided by referring to a previous study,⁸⁾ which treated the base glass (B12, $T_g = 547^\circ\text{C}$) at 683 K (410°C). The glasses were pre-heated to their treatment temperatures minus 30 K, and then dipped into the KNO₃ molten salt bath. After chemical strengthening for 8 h in the salt bath, the glass was cooled to room temperature. The salt on the surface of the glass was rinsed off with water. The CS and DOL were measured by a surface stress meter (Orihara, FSM-60).

For line analysis by an electron probe micro analyzer (EPMA), each glass was sliced along the direction of diffusion. The sample was embedded in epoxy resin, then vacuumed overnight. To exclude the effects of two-dimensional diffusion, each sample was ground and polished to at least 2 mm from the surface, then coated with an ~25 nm-thick gold layer (Sanyu Electron, SC-701AT). The distribution of K in the sliced surface was analyzed by the EPMA (Shimadzu, EPMA-1720) with a beam spot size of ca. 1 μm . The EPMA analysis was combined with wavelength dispersive X-ray spectroscopy. The accelerating voltage and current of the electron beam were 15 kV and 50 nA respectively. In these measurements, the line width was 100–300 μm . Each line was oriented perpendicularly to the direction of diffusion. The characteristic X-ray intensities of K were collected at each step with a preset probe current. The counting time at this current was 0.9 s.

In a simple ion-exchange of two different mobile cations (Na⁺ and K⁺ in this case), the inter-diffusion coefficient $\tilde{D}$ is given by the Nernst–Planck equation:¹⁸⁾

$$\tilde{D} = \frac{D_{\text{Na}} D_{\text{K}}}{D_{\text{Na}} C_{\text{Na}} + D_{\text{K}} C_{\text{K}}}, \quad (6)$$

where D_{Na} and D_{K} are the self-diffusion coefficients of Na⁺ and K⁺ ions, respectively. C_{Na} and C_{K} are the molar fractions of Na⁺ and K⁺ ions, respectively. The inter-diffusion coefficient was determined by fitting the profile to the equation

$$\frac{C_{\text{K},t} - C_{\text{K,min}}}{C_{\text{K,max}} - C_{\text{K,min}}} = \text{erfc}\left(\frac{x}{\sqrt{4\tilde{D}t}}\right), \quad (7)$$

where t is the diffusion time, x is the distance from the glass surface, and $C_{\text{K},t}$ is the concentration of K at time t . $C_{\text{K,min}}$ and $C_{\text{K,max}}$ are the minimum and maximum X-ray intensities in the profile, respectively.

3. Results

The Vickers hardness values, densities, elastic moduli, T_g s, and number of oxygens per unit volume of the prepared glass samples are stated in Table 2. Increasing the B₂O₃ content continuously decreased the Vickers hardness and the elastic modulus. The relationship between B₂O₃ content and T_g is plotted in **Fig. 1**. Note that adding 5% B₂O₃ to the B0 glass decreased the base T_g by 100 K. Thereafter, the change was relatively gradual, but the T_g decreased with increasing B₂O₃ in the glass.

As shown in Table 2, the number of oxygens per volume increased with increasing B₂O₃ content. Such increased atomic-level packing increases the Poisson's ratio of the glass. It is known that the Poisson's ratio affects the cracking of glass during indentation. **Figure 2** relates the crack formation probability to the B₂O₃ content of the prepared glasses. Increasing the B₂O₃ content increased the crack formation probability of the glass before the ion-exchange process. This result is consistent with previous reports, which showed that higher atomic-level packing doesn't permit the permanent densification of glass, rendering it brittle.^{19)–21)}

An example of obtained K⁺ and Na⁺ ion concentration profiles were shown in **Fig. 3**. Case depth is a thickness of the K penetration from the glass surface. The K⁺ ions gradually increased toward the surface whereas the surface

Fig. 1. Relationship between glass transition temperature (T_g) and B₂O₃ content in the glass.

Fig. 2. Relationship between crack formation probability and B₂O₃ content.

Na⁺ ions decreased. As for the absolute value of K⁺ concentration, the K⁺ concentration at the surface seemed to decrease with increasing B₂O₃ content (not shown). However, it was not easy to compare it among glass samples due to uncertainties of the surface position and difficulty in keeping various conditions constant. Thus, the normalized K⁺ concentration profiles are shown in Fig. 4. All of the K⁺ concentration profiles were well fitted by Eq. (7). Examples of the fitting curves are shown in Fig. 5. The DOLs of the samples measured by the surface stress meter are shown in Fig. 6 and listed in Table 2. The DOLs decreased with increasing B₂O₃ content. However, the sample showed relatively lower DOLs than the maxi-

Fig. 3. K and Na concentration profiles of B10 after ion-exchanging at $T_g \times 0.83$ (K) for 8 h.

Fig. 4. K-concentration profiles in all samples after ion exchanging at $T_g \times 0.83$ (K) for 8 h. $C_{K,min}$ and $C_{K,max}$ are the minimum and maximum X-ray intensities in the profiles, respectively.

Fig. 5. Curve fittings (broken lines) to the measured K⁺ ion concentration profiles (solid lines) of B2, B6 and B12.

Fig. 6. Relationship between the depth of the ion-exchange layer (measured by a surface stress meter) and the B₂O₃ content of glass. The value at 0% B₂O₃ is estimated from the K⁺ ion profile.

mum depths shown in Fig. 4. Moreover, the DOL of B0 couldn't be determined. Possible causes of this discrepancy are as follows.

First, measurement targets of the EPMA and the surface stress meter are different. The EPMA measures K concentration, whereas the surface stress meter measures birefringence induced by CS. Since some invaded K⁺ ions exist also in tensile stress region. Second, the algorithm of the estimation of surface stress meter,²²⁾ which is linear approximation. Thus, it cannot follow the real stress profile. Therefore, a new algorithm has been proposed to improve the stress measurement.²³⁾ The third cause is the experimental error. Since the sample with a deeper DOL causes many interferences bands (e.g. >40 bands for B2) in the surface stress meter, there would be an uncertainty to count them with accuracy.

As shown in Fig. 6, the DOL was significantly decreased by adding 2–4 mol % B₂O₃. For instance, from B2 to B6, the DOL degraded from 116 to 51 μm.

To further understand the mechanism of Na⁺/K⁺ inter-diffusion in the ALBS glasses, the inter-diffusion coefficients of selected samples (B2, B6, and B12) were determined at different temperatures. The activation energy E_a of the inter-diffusion coefficient can be estimated by the following equation:

$$\tilde{D} = D_0 \exp\left(\frac{-E_a}{RT}\right), \quad (8)$$

where D_0 is a constant, R is the ideal gas constant, and T is the absolute temperature. The inter-diffusion coefficients of B2, B6, and B12 glasses are plotted against the inverse temperature in Fig. 7, and the estimated E_a values are given in Table 3. Figure 7 and Table 4 also present some reported data for comparison.

4. Discussion

As shown in Table 4, the estimated activation energies of B2, B6, and B12 were 78, 95, and 85 kJ/mol, respectively. There was no obvious relationship or tendency with B₂O₃ content. The obtained activation energies of the B2, B6, B12 glasses were lower than most of the data reported in Table 4. For instance, the reported activation energy of SLS glass is 152 kJ/mol,²⁵⁾ larger than the values obtained in this study. The activation energies of the inter-diffusion are also higher in the reported sodium borosilicate glasses than in our glasses.²⁶⁾ On the other hand, the activation energies of ALS²⁵⁾ and boroaluminosilicate (BAS)²⁹⁾ glasses are 95 and 96 kJ/mol, respectively, comparable with that of B6 in Table 4.

These activation energies suggest that the diffusion mechanism of K⁺/Na⁺ ion-exchange in the present ALBS glasses is independent of B₂O₃ content and similar to that of ALS glass. In other words, the B₂O₃ addition does not

Fig. 7. Temperature dependence of the Na^+/K^+ inter-diffusion coefficient in different glasses (B2, B6, and B12). The compositions and activation energies of the glasses are shown in Table 4. BS: borosilicate, ALS: aluminosilicate, BAS: boroaluminosilicate, SLS: soda-lime silicate.

Table 3. Inter-diffusion coefficients and activation energies of the B2, B6, B12 glasses (the numbers in parentheses are the EPMA measurement errors)

Name	B2	B6	B12
Immersion temp. (°C)	$\bar{D}$ (cm ² /s)		
530	$9.4(\pm 0.5) \times 10^{-10}$	$7.9(\pm 0.2) \times 10^{-10}$	
500	$4.3(\pm 0.3) \times 10^{-10}$	$6.2(\pm 0.6) \times 10^{-10}$	$3.5(\pm 0.2) \times 10^{-10}$
470	$5.3(\pm 0.5) \times 10^{-10}$	$3.0(\pm 0.1) \times 10^{-10}$	$1.6(\pm 0.2) \times 10^{-10}$
440	$3.2(\pm 0.9) \times 10^{-10}$	$1.6(\pm 0.2) \times 10^{-10}$	$1.0(\pm 0.1) \times 10^{-10}$
410	$1.8(\pm 0.1) \times 10^{-10}$	$8.3(\pm 0.2) \times 10^{-11}$	$4.6(\pm 0.3) \times 10^{-11}$
380	$5.5(\pm 0.3) \times 10^{-11}$	$3.8(\pm 0.2) \times 10^{-11}$	$3.0(\pm 0.4) \times 10^{-11}$
350	$3.0(\pm 0.2) \times 10^{-11}$	$1.4(\pm 0.2) \times 10^{-11}$	$1.3(\pm 0.2) \times 10^{-11}$
E_a (kJ/mol)	78.4(±20)	94.7(±6)	84.9(±8)

Table 4. Activation energies of Na^+/K^+ inter-diffusion for various glass compositions

Composition (mol %)	T_g (°C)	E_a (kJ/mol)	Measured range (°C)	Ref. No.
B2	654	78	350–530	
B6	580	95	350–530	
B12	547	85	350–530	
5P ₂ O ₅ –95(0.25Na ₂ O–0.08Al ₂ O ₃ –0.67SiO ₂)	—	81	390–430	24
13.3Na ₂ O–2.4K ₂ O–0.34CaO–5.3MgO–10.3Al ₂ O ₃ –66.8SiO ₂ –1.5Others (ALS)	552*	95	400–500	25
14.3Na ₂ O–12.7CaO–0.16Sr ₂ O ₃ –0.11MgO–0.09BaO–0.98Al ₂ O ₃ –71.4SiO ₂ –0.25Others (SLS)	624*	152	400–500	25
20Na ₂ O–60B ₂ O ₃ –20SiO ₂	508	297	343–475	26
20Na ₂ O–45B ₂ O ₃ –35SiO ₂	545	198	343–475	26
20Na ₂ O–30B ₂ O ₃ –50SiO ₂	577	172	343–500	26
20Na ₂ O–15B ₂ O ₃ –65SiO ₂ (BS-4)	600	136	343–475	26
16.1Na ₂ O–16.1MgO–67.8SiO ₂	536*	156	420–490	27
12.9Na ₂ O–2.9K ₂ O–15.8MgO–68.4SiO ₂	527*	143	420–490	27
10.6Na ₂ O–4.7K ₂ O–15.9MgO–68.8SiO ₂	536*	138	420–490	27
7.8Na ₂ O–7.8K ₂ O–15.6MgO–68.9SiO ₂	542*	129	420–490	27
5.4Na ₂ O–10.2K ₂ O–16.9MgO–67.5SiO ₂	562*	122	420–490	27
4.7Na ₂ O–8.5K ₂ O–26.6PbO–57.6SiO ₂ –2.6Others (wt %)	445	129	350–430	28
12Na ₂ O–6MgO–6B ₂ O ₃ –15Al ₂ O ₃ –61SiO ₂ (BAS)	—	96	370–450	29

*Annealing point is stated when T_g data are lacking.

Fig. 8. Relationship between Na⁺/K⁺ inter-diffusion coefficient and the number of oxygens per unit volume. The ion-exchange condition of each sample was ($T_g \times 0.83$) K for 8 h.

disturb the fast-transport path-ways near the AlO₄[−] units. As is well known, the alkali ions in ALBS are preferentially used as charge compensators for the AlO₄[−] units.^{30),31)} Thus, the alkali ions in the present glasses mainly passed near the AlO₄[−] units in the Al^{IV}–O–Si continuous network, where Al^{IV} denotes four-fold oxygen coordinated Al.

In the glass compositions of the present study, the number ratio of aluminum ions to the total former cations (B³⁺, Al³⁺, Si⁴⁺) was larger than one-third. This implies that each SiO₄ unit had at least one AlO₄[−] neighbor and that the alkali path-way may have remained intact. It also confirms that the major alkali path-way was unchanged by the B₂O₃ content. In alkaline-earth sodium boroaluminosilicate glasses,²⁹⁾ the Na⁺/K⁺ inter-diffusion coefficient is maximized when [Na₂O] = [Al₂O₃], as also observed in ALS glass. Furthermore, the mobility of the sodium ions in sodium boroaluminosilicate³²⁾ decreases with increasing [SiO₂]/[Al₂O₃] ratio, or with increasing NBOs in the glass. As the glasses in this study contained an adequate number of AlO₄[−] units, they likely formed similar alkali path-ways nearby the AlO₄[−] units. These similar path-ways probably explain the very similar activation energies of inter-diffusion among the samples.

According to the Anderson and Stuart model,³³⁾ the activation energy of alkali diffusion in glass is contributed by two parts: the elastic strain energy of enlarging a doorway to neighboring sites, and the electrostatic energy between the alkali ions and the negatively charged units. The former effect was probably not large in the present case, because the activation energy did not depend on the glass composition, but the shear modulus was 12% smaller for B12 glass than for B2 glass. The shear modulus of glass is directly proportional to the elastic strain energy of opening doorways.³³⁾ Therefore, the similar activation energies obtained in this study support the assumption of constant coulomb interaction energies between the alkaline ions and their neighboring anions (namely, the AlO₄[−] units) in the glasses.

Despite the comparable activation energies among these glasses, their inter-diffusion coefficients decreased with increasing B₂O₃ content (Table 2). The same trend was reported in a previous paper,³⁴⁾ which investigated the inter-diffusion coefficients of Na⁺/K⁺ ion-exchange in soda-lime borosilicate glasses [(74 − *x*)SiO₂ − *x*B₂O₃ − 15Na₂O − 10CaO − 1Fe₂O₃, *x* = 0 to 74]. The authors of the soda-lime borosilicate study³⁴⁾ considered that as the B₂O₃ content increases, the isothermal inter-diffusion coefficient is reduced by the lower partial molar volume of boron-related structures such as BO₄[−], which increase the atomic-level packing. Vacancies and interstitial sites are very important for ion-diffusion in both crystals and glasses.³⁵⁾ Increasing the number of interstitial (and/or vacancy) sites for a given ion will increase the diffusion coefficient of the ion.

Although this interstitial diffusion mechanism is not easily applicable to Na⁺/K⁺ inter-diffusion in multi-component glasses, increasing the free volume obviously increases the number of vacancies or interstitial sites. Therefore, one can deduce that the atomic-level packing, or free volume, is closely related to the inter-diffusion coefficient. The negative relationship between the inter-diffusion coefficient and atomic packing factor (see Fig. 8) confirms this assumption. The B₂O₃ addition narrows the ion channels, thereby decreasing the diffusion coefficient. If this structural change does not affect the elastic strain energy of opening the alkali path-way, the activation energy will remain largely unchanged, as shown in Table 4. How the boron-related sub-structures, which may be involved in crack resistance (as shown below), affect the inter-diffusion in glass remains unclear. The detailed atomistic mechanism of alkali transportation in boron-containing glass is left open for future consideration.

In the glasses prepared in this study, the total alkali oxide content (Na₂O + K₂O) was ~18 mol % and the Al₂O₃ content was ~16 mol %. As stated above, most of the alkali ions compensated the charge of the AlO₄[−] units.

The remaining alkali ions created NBOs or compensated the charge of BO_4^- units. Thus, increasing the B_2O_3 content from 0 mol % (B0) to 16 mol % (B16) would increase the three-fold coordinated boron. As confirmed in our previous study⁸⁾ and in Fig. 2 of the present study, the crack formation probability before the ion-exchange increases with B_2O_3 content. In other words, the B_2O_3 -containing glass is brittle against Vickers indentation. This behavior can be attributed to the increased packing density, and is also related to sub-structural changes. A Raman spectroscopic analysis⁸⁾ reported that increasing the B_2O_3 content induces a structural change from a reedmergnerite ring (three SiO_2 and one BO_4 tetrahedra) to triborate (one BO_4 tetrahedron and two BO_3 triangles). Such changes in the boron-related sub-structure should be considered when selecting glass compositions with improved ion-exchange and mechanical properties.

From an industrial viewpoint, the ALBS glasses investigated in this study require a high Na^+/K^+ inter-diffusion coefficient during the ion-exchange process, and a low activation energy of diffusion. These properties are important because adding B_2O_3 can reduce the energy of melting the batch. Indeed, adding 6 mol % B_2O_3 decreased the T_g by 100 K. However, the B_2O_3 addition also increased the crack formation probability before the ion-exchange, which degraded the hardness and elastic modulus of the glass (Table 2). It appears that a B_2O_3 content of 4–6% is an effective compromise for ensuring high productivity, ion-exchange rate (or DOL), and mechanical properties of the raw glass.

5. Conclusions

This study investigated the effect of B_2O_3 content on the ion diffusivity in ALBS glasses. Increasing the B_2O_3 content significantly decreased both the DOL and the Na^+/K^+ inter-diffusion coefficient, suggesting that B_2O_3 reduces the ion-exchange rate of the glass. On the other hand, the activation energies derived from Arrhenius plots of the inter-diffusion coefficients were seemingly independent of the B_2O_3 content in the glass. The decreased inter-diffusion coefficient at higher B_2O_3 contents can be explained by the increased atomic-level packing, which inhibits the mobility of the ions. Dense atomic-layer packing also increases the crack forming probability by increasing the number density of oxygen ions in the glass. Considering the melting temperature, the ion-exchange rate, and the mechanical properties, the addition of 4–6 mol % B_2O_3 maximally improved the chemical strengthening of the ALS base glass.

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