Effect of B$_2$O$_3$ substitution for SiO$_2$ in alkali aluminoborosilicate glasses on chemical strengthening

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This study reports the strengthening effect of partially substituting SiO$_2$ with B$_2$O$_3$ in aluminoborosilicate (ALBS) glasses. Specifically, it investigates how the B$_2$O$_3$ addition affects the ion-exchange behavior of the glass. The base composition of ALBS glass is 13Na$_2$O–5K$_2$O–7MgO–15Al$_2$O$_3$–12B$_2$O$_3$–48SiO$_2$ (mol %). In the prepared samples, the proportion of B$_2$O$_3$ 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 KNO$_3$ at ($T_g$ × 0.83) K (where $T_g$ is the glass transition temperature) for 8 h. Adding only a small amount of B$_2$O$_3$ drastically changed the K$^+$ ion concentration profile. In contrast, the activation energy of the Na$^+$/$K^+$ inter-diffusion was almost independent of B$_2$O$_3$ content. These results suggest that the B$_2$O$_3$ 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.$^{1,3}$ 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.$^{3,6}$ For this reason, a high CS requires either a quick ion-exchange or a short immersion time in the molten KNO$_3$ 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 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 Na$_2$O/Al$_2$O$_3$ = 1.0.$^{14}$ The sodium ions in this composition predominately act as charge compensators of the AlO$_4$– units, and are more easily moved than those bonding with NBOs.$^5$ After immersion at 410°C for 8 h in a molten KNO$_3$ bath, the DOL is only 12 μm.$^9$ 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.$^9$ 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.$^6$

The melting temperature can be reduced by adding B$_2$O$_3$ as a flux component. The B$_2$O$_3$ lowers the temper-
nature of the batch reactions, so the Al2O3-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 B2O3 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 B2O3 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 B2O3 in chemical strengthening, have been rarely reported.

To elucidate these phenomena, the present study evaluates the effect of the B2O3 content in ALBS glass on the ion-exchange mechanism.

2. Experimental procedures

The base glass composition in this study was 13Na2O-5K2O-7MgO-15Al2O3-12B2O3-48SiO2 (mol %), as reported in a previous study.8,17) The B2O3 content of the glass was varied from 0 to 16 mol % in 2 mol % steps (see Table 1). The B2O3 component partially replaced the SiO2 in the base glass composition. In Table 1, the number in the sample name denotes the molar content of B2O3; for example, B12 denotes that the glass contains 12 mol % of B2O3 in the batch. Batches of 500-g glasses were prepared from reagent-grade powders of Na2CO3, NaNO3, K2CO3, KNO3, MgO, Na2B4O7, Al(OH)3, and SiO2. 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 [(Tg + 30) K, where Tg is the glass transition temperature], held for 30 min, and then cooled at 3 K/min to obtain annealed glasses. The Tg 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 B2O3 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 (N0, 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
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.\(^9\)

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 Ultrasound). The longitudinal and shear wave sound velocities \((V_l, V_s)\) of the sample were measured using different transducers. Each velocity was determined from the sample thickness \(d\) and the round trip transit time \(s\), as follows:

\[
V_l = \frac{2d}{s}
\]

\[
V_s = \frac{2d}{s}
\]

(1)

The Young’s modulus \((E)\) was calculated from the density \(\rho\) and the longitudinal and shear wave sound velocities:

\[
E = \frac{V_l^2}{\rho} - \frac{4V_s^2}{V_l^2 - V_s^2}
\]

(2)

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

\[
G = \nu V_s^2
\]

\[
\nu = \frac{1}{2} \left( \frac{V_l^2 - 2V_s^2}{V_l^2} \right)
\]

\[
K = \frac{E}{3(1 - 2\nu)}
\]

(3)

(4)

(5)

The glass samples were chemically strengthened by ion-exchange in KNO\(_3\) 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,\(^9\) which treated the base glass \((B12, T_g = 547^\circ C)\) at 683 K \((410^\circ C)\). The glasses were pre-heated to their treatment temperatures minus 30 K, and then dipped into the KNO\(_3\) 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 \(\mu m\). 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 \(\mu m\). 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 \(\bar{D}\) is given by the Nernst–Planck equation:\(^{18}\)

\[
\bar{D} = \frac{D_{Na}D_{K}}{D_{Na}C_{Na} + D_{K}C_{K}}
\]

(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 \(C_{K}\) was determined by fitting the profile to the equation

\[
\frac{C_{K} - C_{K,min}}{C_{K,max} - C_{K,min}} = \text{erf} \left( \frac{x}{\sqrt{4D_{t}t}} \right)
\]

(7)

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

3. Results

The Vickers hardness values, densities, elastic moduli, \(T_g\), and number of oxygens per unit volume of the prepared glass samples are stated in Table 2. Increasing the B\(_2\)O\(_3\) content continuously decreased the Vickers hardness and the elastic modulus. The relationship between B\(_2\)O\(_3\) content and \(T_g\) is plotted in Fig. 1. Note that adding 5% B\(_2\)O\(_3\) 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 B\(_2\)O\(_3\) in the glass.

As shown in Table 2, the number of oxygens per volume increased with increasing B\(_2\)O\(_3\) content. Such increased atomic-level packing increases the Poisson’s ratio of the glass. It is known that the Poisson’s ratio affects the breaking strength of glass during indentation. Figure 2 relates the crack formation probability to the B\(_2\)O\(_3\) content of the prepared glasses. Increasing the B\(_2\)O\(_3\) 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
Na\(^+\) ions decreased. As for the absolute value of K\(^+\) concentration, the K\(^+\) concentration at the surface seemed to decrease with increasing B\(_2\)O\(_3\) 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 B\(_2\)O\(_3\) content. However, the sample showed relatively lower DOLs than the maxi-
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\textsuperscript+ ions exist also in tensile stress region. Second, the algorithm of the estimation of surface stress meter\textsuperscript{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.\textsuperscript{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% B\textsubscript{2}O\textsubscript{3}. For instance, from B2 to B6, the DOL degraded from 116 to 51 μm.

Fig. 5. Curve fittings (broken lines) to the measured K\textsuperscript+ 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 B\textsubscript{2}O\textsubscript{3} content of glass. The value at 0% B\textsubscript{2}O\textsubscript{3} is estimated from the K\textsuperscript+ ion profile.

To further understand the mechanism of Na\textsuperscript+\texttwoversus K\textsuperscript+ 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:

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

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 B\textsubscript{2}O\textsubscript{3} 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,\textsuperscript{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.\textsuperscript{26} On the other hand, the activation energies of ALS\textsuperscript{25} and boroaluminosilicate (BAS)\textsuperscript{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\textsuperscript+\texttwoversus Na\textsuperscript+ ion-exchange in the present ALBS glasses is independent of B\textsubscript{2}O\textsubscript{3} content and similar to that of ALS glass. In other words, the B\textsubscript{2}O\textsubscript{3} 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  | Immersion temp. (°C) | \(D\) (cm\(^2\)/s) | \(E_a\) (kJ/mol) |
|-------|----------------------|----------------------|------------------|
| B2    | 530                  | 9.4(±0.5) \(\times 10^{-10}\) | 78.4(±20)        |
|       | 500                  | 4.3(±0.3) \(\times 10^{-10}\) | 94.7(±6)         |
|       | 470                  | 5.3(±0.5) \(\times 10^{-10}\) | 84.9(±8)         |
|       | 440                  | 3.2(±0.9) \(\times 10^{-10}\) |                |
|       | 410                  | 1.8(±0.1) \(\times 10^{-10}\) |                |
|       | 380                  | 5.5(±0.3) \(\times 10^{-11}\) |                |
|       | 350                  | 3.0(±0.2) \(\times 10^{-11}\) |                |

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

| Composition | \(T_g\) (°C) | \(E_a\) (kJ/mol) | Measured range (°C) | Ref. No. |
|-------------|--------------|------------------|----------------------|----------|
| B2          | 654          | 78               | 350-530              | 24       |
| B6          | 580          | 95               | 350-530              | 25       |
| B12         | 547          | 85               | 350-530              |          |
| B2          | 530          | 9.4(±0.5) \(\times 10^{-10}\) | 78.4(±20)        |
| B6          | 500          | 4.3(±0.3) \(\times 10^{-10}\) | 94.7(±6)         |
| B12         | 470          | 5.3(±0.5) \(\times 10^{-10}\) | 84.9(±8)         |
| B2          | 440          | 3.2(±0.9) \(\times 10^{-10}\) |                |
| B6          | 410          | 1.8(±0.1) \(\times 10^{-10}\) |                |
| B12         | 380          | 5.5(±0.3) \(\times 10^{-11}\) |                |
| B2          | 350          | 3.0(±0.2) \(\times 10^{-11}\) |                |

*Annealing point is stated when \(T_g\) data are lacking.
disturb the fast-transport path-ways near the AlO$_4^-$ units. As is well known, the alkali ions in ALBS are preferentially used as charge compensators for the AlO$_4^-$ units $^{30,31}$ Thus, the alkali ions in the present glasses mainly passed near the AlO$_4^-$ 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 ($B^3+$, $Al^{3+}$, $Si^{4+}$) was larger than one-third. This implies that each SiO$_2$ unit had at least one AlO$_4^-$ neighbor and that the alkali path-way may have remained intact. It also confirms that the major alkali path-way was unchanged by the B$_2$O$_3$ content. In alkaline-earth sodium borosilicate glasses, $^{29}$ the Na$^+$/K$^+$ inter-diffusion coefficient is maximized when [Na$_2$O] = [Al$_2$O$_3$], as also observed in ALS glass. Furthermore, the mobility of the sodium ions in sodium borosilicate glasses $^{23}$ decreases with increasing [SiO$_2$]/[Al$_2$O$_3$] ratio, or with increasing NBOs in the glass. As the glasses in this study contained an adequate number of AlO$_4^-$ units, they likely formed similar alkali path-ways nearby the AlO$_4^-$ 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 alkali ions and their neighboring anions (namely, the AlO$_4^-$ units) in the glasses.

Despite the comparable activation energies among these glasses, their inter-diffusion coefficients decreased with increasing B$_2$O$_3$ 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)SiO$_2$–xB$_2$O$_3$–15Na$_2$O–10CaO–1Fe$_2$O$_3$, x = 0 to 74]. The authors of the soda-lime borosilicate study $^{34}$ considered that as the B$_2$O$_3$ content increases, the isothermal inter-diffusion coefficient is reduced by the lower partial molar volume of boron-related structures such as BO$_4^-$, 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 B$_2$O$_3$ 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 (Na$_2$O + K$_2$O) was ~18 mol% and the Al$_2$O$_3$ content was ~16 mol%. As stated above, most of the alkali ions compensated the charge of the AlO$_4^-$ units.

![Fig. 8. Relationship between Na$^+$/K$^+$ inter-diffusion coefficient and the number of oxygens per unit volume.](image)

The ion-exchange condition of each sample was (T$_g$ x 0.83) K for 8 h.
The remaining alkali ions created NBOs or compensated the charge of BO$_3^-$ units. Thus, increasing the B$_2$O$_3$ content from 0 mol % (B0) to 16 mol % (B16) would increase the three-fold coordinated boron. As confirmed in our previous study$^9$ and in Fig. 2 of the present study, the crack formation probability before the ion-exchange increases with B$_2$O$_3$ content. In other words, the B$_2$O$_3$-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 analysis$^9$ reported that increasing the B$_2$O$_3$ 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$_2$O$_3$ can reduce the energy of melting the batch. Indeed, adding 6 mol % B$_2$O$_3$ decreased the T$_g$ by 100 K. However, the B$_2$O$_3$ 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$_2$O$_3$ 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$_2$O$_3$ content on the ion diffusivity in ALBS glasses. Increasing the B$_2$O$_3$ content significantly decreased both the DOL and the Na$^+/K^+$ inter-diffusion coefficient, suggesting that B$_2$O$_3$ 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$_2$O$_3$ content in the glass. The decreased inter-diffusion coefficient at higher B$_2$O$_3$ 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 formation 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$_2$O$_3$ maximally improved the chemical strengthening of the ALS base glass.

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