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Competitive Effects of Free Volume, Rigidity, and Self-Adaptivity on Indentation Response of Silicoaluminoborate Glasses

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Abstract: Lithium aluminoborate glasses have recently been found to feature high resistance to crack initiation during indentation, but suffer from relatively low hardness and chemical durability. To further understand the mechanical properties of this glass family and their correlation with the network structure, we here study the effect of adding SiO₂ to a 25Li₂O-20Al₂O₃-55B₂O₃ glass on the structure and mechanical properties. Addition of silica increases the average network rigidity, but meanwhile its open tetrahedral structure decreases the atomic packing density. Consequently, we only observe a minor increase in hardness and glass transition temperature, and a decrease in Poisson's ratio. The addition of SiO₂, and thus removal of Al₂O₃ and/or B₂O₃, also makes the network less structurally-adaptive to applied stress, since Al and B easily increase their coordination number under pressure, while this is not the case for Si under modest pressures. As such, although the silica-containing networks have more free volume, they cannot densify more during indentation, which in

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turn leads to an overall decrease in crack resistance upon SiO₂ addition. Our work shows that, although pure silica glass has very high glass transition temperature and relatively high hardness, its addition in oxide glasses does not necessarily lead to significant increase in these properties due to the complex structural interactions in mixed network former glasses and the competitive effects of free volume and network rigidity.

1. Introduction

Oxide glasses play a critical role for innovation in a range of industries due to their combination of properties such as transparency, high hardness, relatively light weight, and chemical durability¹. However, these materials are brittle since they lack a stable shearing mechanism. The practical strength of glass is also low due to the presence of surface flaws and defects, which act to amplify local tensile stresses, resulting in catastrophic failures^{2,3}. This obviously limits many industrial applications within energy, medicine, consumer electronics, etc. There is thus a need to develop new glasses with higher inherent damage or crack resistance in order to minimize the number of cracks and their propensity to propagate from flaws, e.g., created during handling. To achieve this aim, various extrinsic post-treatment methods have been used in oxide glasses, such as chemical strengthening that result in the formation of a compressive stress layer at the surface, thereby limiting any propagating cracks⁴. However, post-processing is expensive and consistently accompanied by undesirable side effects^{5,6}. Therefore, there is an increasing interest in enhancing the inherent mechanical properties of oxide glass by a rational design of the chemical composition⁷.

Recent progress has been made in the area of composition design by focusing on controlling the network topology (e.g., through mixed network formers or modifiers) and the resulting deformation mechanism. This has led to the discovery of various glass families with high inherent damage resistance, including mixed modifier aluminosilicate⁸, binary aluminosilicate⁹, calcium boroaluminosilicate¹⁰, tantalum aluminate¹¹, and alkali aluminoborate compositions^{12,13}. In these previous works, the damage resistance has been evaluated using instrumented indentation, since sharp contact is the primary failure mode of glasses for many applications. Indentation thus mimics real-life damage incidents under controlled conditions, requiring relatively small sample area and with short

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experiment time^{14,15}. However, we note that it is important to distinguish between resistance to crack initiation and crack growth, as high crack initiation resistance (which is measured by indentation) does not necessarily entail large fracture toughness¹⁶. By studying different glass compositions, Peter showed that the deformation mechanism of oxide glasses to indentation in general includes both densification and shear flow¹⁷. Kato *et al.* have shown that glass compositions prone to undergo densification during indentation can lower the residual stress acting as the driving for cracking, since densification does not lead to an expansion of the plastic zone¹⁸. This can in turn be achieved by producing glasses with high levels of free volume within their atomic network⁸, designing self-adaptive networks where structural rearrangements promote densification¹², or controlling rigidity fluctuations on the nano-scale¹⁹. However, more understanding is needed to properly link glass chemistry and network structure with the indentation deformation mechanism and cracking resistance.

In this work, we build on the recent progress made in achieving high crack resistance in alkali aluminoborate glasses^{13,20,21}. Specifically, we discovered a melt-quenchable lithium aluminoborate glass with very high resistance to indentation cracking, i.e., Vickers indentation loads close to 2 kgf (~20 N) are needed to induce radial cracking¹². Structural analyses revealed that the coordination numbers of both boron and aluminum in this glass increase dramatically upon densification, e.g., the average Al coordination number increases from 4.29 to 4.85 upon hot compression at 2 GPa. These structural changes and volume densification manifest themselves in record-high (compared to previously studied oxide glasses) pressure-induced changes in material properties, such as Vickers hardness and Young's modulus. On the basis of the pressure dependence of density and the short-range order of boron and aluminum, we have introduced a new parameter (atomic self-adaptivity) for understanding high crack resistance in oxide glasses. High self-adaptivity corresponds to large pressure-driven changes in density and coordination numbers of the network formers.¹² Future applications of the lithium aluminoborate glass are, however, limited by its relatively low hardness²¹ and chemical durability²².

To further understand the mechanical properties of this glass family and their correlation with the network structure, we study the effect of adding SiO₂ (up to 20 mol%) to a 25Li₂O-20Al₂O₃-55B₂O₃ glass on the structure and mechanical properties. SiO₂ addition is interesting to explore, since

pure silica glass features relatively high values of glass transition temperature, hardness, and chemical durability^{23,24}. We refer to the present glasses as silicoaluminoborates, since B₂O₃ remains the major network-forming oxide, unlike typical aluminoborosilicate glasses with SiO₂ content above, e.g., 50 mol%^{25,26,27}. In previous related work, Morin *et al.* have found that the glass transition temperature (T_g) of modified SiO₂-Al₂O₃-B₂O₃ glasses with relatively small SiO₂ content is mostly controlled by modifier cation-oxygen bond strength, and not to Al and B coordination²⁸. Besides, Khanna *et al.* have shown that increase of silica concentration suppresses the concentration of five- and six-fold Al in bismuth aluminoborate glasses²⁹. In this study, we synthesize two glass series, in which we keep the Li/Al ratio constant. This is done to keep the structural role of Al approximately constant, since it has a strong enthalpic preference for being charge-stabilized by alkali cations (e.g., Li⁺) in tetrahedral configuration¹². In the first series, SiO₂ is added while the remaining components are scaled down proportionally: $x\text{SiO}_2-(1-x)[25\text{Li}_2\text{O}-20\text{Al}_2\text{O}_3-55\text{B}_2\text{O}_3]$. In the second series, SiO₂ is substituted for B₂O₃: $y\text{SiO}_2-25\text{Li}_2\text{O}-20\text{Al}_2\text{O}_3-(55-y)\text{B}_2\text{O}_3$. For both series, we investigate the effect of the SiO₂ doping on glass transition temperature, density, structure (as probed by Raman spectroscopy), hardness, elastic moduli, indentation deformation mechanism, and crack resistance.

2. Experimental

2.1 Glass preparation

We prepared two series of lithium silicoaluminoborate glasses using the traditional melt-quenching technique. That is, $x\text{SiO}_2-(1-x)[25\text{Li}_2\text{O}-20\text{Al}_2\text{O}_3-55\text{B}_2\text{O}_3]$ (named x -series) with $x = \{2,5,10,20\}$ and $y\text{SiO}_2-25\text{Li}_2\text{O}-20\text{Al}_2\text{O}_3-(55-y)\text{B}_2\text{O}_3$ (named y -series) with $y = \{2,5,10,20\}$ (in mol%). We also synthesized the base lithium aluminoborate glass with $x = y = 0$. The nominal chemical compositions of the glasses is shown in Table S1 in the Supporting Information. The utilized raw materials were Li₂CO₃ (≥98.5%, Merck KGaA), Al₂O₃ (99.5%, Sigma-Aldrich), H₃BO₃ (≥99.5%, Honeywell International), and SiO₂ (≥99.5%, 0.2-0.8 mm, Merck KGaA). First, according to the target composition, all raw materials were weighed and thoroughly mixed. The mixed batch materials were then stepwise added to a Pt-Rh crucible in a furnace at 800 °C to remove H₂O and CO₂. Subsequently, the batch was melted at 1400 °C for 2 hours in air, where after the melt was poured onto a steel plate

for quenching. The obtained glasses were quickly transferred to a preheated annealing furnace at an estimated glass transition temperature (T_g) value based on the previous studies¹². X-ray diffraction (XRD) patterns of the specimens were acquired (Empyrean XRD, PANalytical) from 0° to 70° at 40 kV with a scanning speed of 8°/min. As shown in Figure S1 in the Supporting Information, none of the samples show any signs of crystallization.

We determined T_g of the glasses from differential scanning calorimetry measurements (STA 449 F3 Jupiter, Netzsch) at 10 K/min on specimens with a known thermal history (i.e., with a preceding cooling rate of 10 K/min). T_g values and other property data are summarized in Table S2 in the Supporting Information. These samples were analyzed using Pt crucible in argon (gas flow 60 mL/min). The recorded heat flow curves are shown in Figure S2 in the Supporting Information. The intercept between the tangent to the inflection point of the endothermic peak and the extrapolated heat flow of the glass was interpreted as the onset of the glass transition. Following determination of T_g , the glasses were reannealed for 0.5 h at their measured T_g value and cooled down to room temperature at a cooling rate of approximately 3 K/min. After re-annealing, all the glasses were cut into desired dimensions for density, modulus, Raman, and indentation experiments, and then optically polished in ethanol using diamond grinding disks.

2.2 Density

Density (ρ) of the glass specimens was determined using Archimedes' principle of buoyancy. The weight of each specimen (at least 1.5 g) was measured in air and ethanol ten times. Based on the ratio between molar mass and density, we calculate the molar volume (V_m). To also quantify differences in free volume among the different glasses, we calculate the atomic packing density (C_g) based on these data. This was done by assuming 6-fold coordination for Li, 2-fold coordination for O, 4-fold coordination for Si, 83% 3-fold and 17% 4-fold coordination for B, and 74% 4-fold, 23% 5-fold and 3% 6-fold coordination for Al¹². The boron and aluminum speciation is based on previous structural work on the lithium aluminoborate glass with $x = y = 0$,¹² but we note that the C_g values are relatively insensitive to those speciation fractions. C_g is defined as the ratio between the theoretical molar volume occupied by the ions and the effective molar volume of the glass,

$$C_g = \rho \frac{\sum f_i V_i}{\sum f_i M_i}$$

(1)

Here, $V_i = \frac{4}{3}\pi N(xr_A^3 + yr_B^3)$ represents the molar volume of an oxide A_xB_y with the molar fraction f_i and the molar mass M_i , N denotes the Avogadro number, and r_A and r_B of are the ionic radii of the cations and anions, respectively, which are taken from Shannon³⁰.

2.3 Elastic moduli

The elastic properties of the glasses were measured by ultrasonic echography using an ultrasonic thickness gauge (38DL Plus, Olympus) equipped with 20 MHz delay line transducers for the determination of the longitudinal V_1 and transversal wave velocities V_2 . The longitudinal modulus C_{11} , shear modulus G , bulk modulus B , and Young's modulus E as well as the Poisson ratio ν were calculated using the following relations, which are applicable for isotropic materials:

$$C_{11} = \rho V_1^2,$$

(2)

$$G = \rho V_2^2,$$

(3)

$$B = C_{11} - \frac{4}{3}G,$$

(4)

$$\nu = \frac{3B-2G}{6B+2G},$$

(5)

$$E = 2G(1 + \nu).$$

(6)

2.4 Raman spectroscopy

Raman spectra were collected using a micro-Raman spectrometer (inVia, Renishaw). The sample surface was excited by a 532 nm green HeNe laser for an acquisition time of 10 s. The range of the spectrum was from 250 to 1750 cm^{-1} and the resolution was better than 2 cm^{-1} . Spectra from five different locations on the glass were accumulated for each specimen to ensure homogeneity. All spectra were uniformly treated in Origin software for background correction and area normalization.

2.5 Vickers micro-indentation

We determined the Vickers hardness (H_V) using a Nanovea CB500 hardness tester. On each specimen, 20 indents with a maximum load of 9.8 N (1 kgf) were generated. The loading duration and dwell time were set to 15 s and 10 s, respectively. The residual imprints were subsequently analyzed with an optical microscope and H_V was calculated as,

$$H_V = 1.8544 \frac{P}{\left(\frac{d_1+d_2}{2}\right)^2},$$

(7)

where P is the contact load, and d_1 and d_2 are the length of the projected indent diagonals.

Vickers indentation was also used to evaluate the crack resistance (CR), i.e., the resistance of the glass towards radial crack initiation upon indentation. For this purpose, the glass specimens were indented with stepwise increasing loads (from 2 to 42 N), and the numbers of radial cracks emanating from the corners of the residual imprints were counted. Following the method of Wada³¹, the probability of crack initiation (PCI) was derived as the ratio between the number of corners, where a corner crack was formed and the total number of corners on all indents. The crack resistance is defined as the load at which an average of two cracks (PCI =50%) occurred. On every specimen, at least 30 indents were made with loading durations of 15 s and dwell times of 10 s. The measurements were conducted at laboratory conditions (room temperature, relative humidity ~25% RH). The cracks were counted 2 h after unloading.

In order to evaluate the indentation deformation mechanism of the glasses, we determined the recovery of the indent side length. This approach consists of recording topographic images of the indent site before and after a thermal treatment at $0.9T_g$ for 2 h²³, which is used to measure how much the side length of indent cavity shrinks upon annealing. On every specimen, we analyzed at least 10 indents with a load of 4 N, loading duration of 15 s and dwell time of 10 s. The indentation side length, $L_{s,i}$, was determined from the optical microscope. After annealing, the indentation side length, now $L_{s,f}$, was determined again. Similarly to the recovery of indentation volume following Yoshida's method²³, the contribution of densification to the overall indentation deformation is estimated from the temperature-induced side length recovery (L_{SR}),

$$L_{SR} = \frac{L_{s,i} - L_{s,f}}{L_{s,i}}$$

(8)

3. Results and discussion

3.1 Raman spectroscopy

Structural changes due to silica addition in the lithium aluminoborate glasses are investigated by Raman spectroscopy (Fig. 1). The spectrum exhibits many features characteristic of alkali borate glasses, but additional bands from other structural units are also observed. We divide the spectrum into five main bands enumerated I through V, with the expected assignments outlined in the following. All expected band assignments are summarized in Table S3 in the Supporting Information.

Band region I (~ 280 to 625 cm^{-1}) is expected to contain contributions originating from B-O-B, Al-O-Al, and B-O-Al stretching²⁶. Besides, vibrations due to superstructural units such as pentaborates may occur in this region. Furthermore, Si-O-Si network units may also occur in this region²⁶. We find that the relative intensity of this band region increases with the content of SiO_2 for both series of glasses. Finally, we also note a small sharp peak in band region I, indicating a minor degree of crystallization although not detectable by XRD. Band region II (~ 625 to 815 cm^{-1}) is characteristic for B_2O_3 -rich glasses²⁶, since peaks in this frequency range are typically assigned to borate super-structures such as chain and ring metaborates^{32,33}, di-triborates³⁴, and penta-, tetra-, or

triborates^{32,33,34,35}, as well as boroxol rings^{32,36}. In addition, B-O-Al stretching and aluminate network may occur in this region. For the *x*-series glasses where SiO₂ is added and other oxides are scaled down proportionally, there is no significant compositional change in this band region. However, it decreases in intensity with the content of SiO₂ increasing for the *y*-series glasses with Si-for-B substitution, since the addition of SiO₂, and thus removal of B₂O₃, must decrease the probability of forming medium-range order borate super-structures.

Band region III (~815 to 1000 cm⁻¹) is expected to result from vibrations of AlO₄ units (~900 cm⁻¹)^{37,38}, Al-B network (~980 cm⁻¹)²⁷ and borate superstructures (~930 cm⁻¹)^{26,33}. For both series of glasses, this band region decreases in intensity with the content of SiO₂. Band region IV (~900 to 1150 cm⁻¹) is expected to contain contributions originating from the *Qⁿ* species (SiO₄ units with *n* bridging oxygen)²⁶ with bands at 1000 and 1150 cm⁻¹ attributed to the stretching Si-O vibration in *Q²* and *Q³* species²⁷, respectively. Furthermore, intermediate bands at 900-940 cm⁻¹ are indication of Si-O-Al network³⁹. For the *x*-series glasses where SiO₂ is added and other oxides are scaled down proportionally, this peak increases slightly in intensity with the content of SiO₂. However, it increases significantly in intensity with the content of SiO₂ increasing for the *y*-series glasses with Si-for-B substitution, since the addition of SiO₂, and thus removal of B₂O₃, must decrease the fraction of the Al-O-B network, leading to more Si-O-Al bonds.

Finally, band region V (~1150 to 1600 cm⁻¹) is expected to be dominated by signal contributions from vibrations of superstructural units such as pyroborate units, chain and ring metaborate units⁴⁰. For the *x*-series glasses where SiO₂ is added and other oxides are scaled down proportionally, there is no significant compositional change in this band region. However, it decreases in intensity with the content of SiO₂ increasing for the *y*-series glasses with Si-for-B substitution, since the addition of SiO₂, and thus removal of B₂O₃, must decrease the fraction of borate superstructures.

3.2 Atomic packing and network rigidity

Figure 2 shows the composition dependence of density (ρ), molar volume (V_m), and atomic packing density (C_g) for the two series of lithium silicoaluminoborate glasses. Addition of SiO_2 has only a minor effect on density when the other components are scaled down proportionally, whereas for the y -series of glasses, the density increases monotonically with the content of SiO_2 . However, since the molar mass is also changing with composition, we calculate the molar volume to evaluate changes in overall network packing. For both series, V_m decreases with the content of SiO_2 , showing that the glass network takes up less volume per mol of glass after silica addition. However, since there are also changes in the size of the atoms, we finally calculated the atomic packing density to understand differences in free volume. C_g also decreases with the content of SiO_2 for both series. This result shows that the network becomes gradually more open with silica addition, almost independent of how silica is added, since the two curves almost overlap in Figure 2. This is consistent with the open microstructure of pure silica glass.

To quantify changes in network connectivity upon silica introduction into the glasses, we use topological constraint theory^{41,42,43,44,45} to enumerate the number of bond constraints per atom (n_c). Chemical bonds and bond angles constrain atoms in network glasses, with the strengths of the constraints depending on the local topology and the chemical nature of elements. Building on knowledge of the atomic coordination numbers (CN) of the network formers, we can compute the total number of linear-bond stretching ($n_{c,\text{linear}} = \text{CN}/2$) and angular-bond bending ($n_{c,\text{angular}} = 2\text{CN} - 3$) constraints for each network-forming atom, in addition to any constraints on the network modifiers⁴⁶.

For the present glasses, we estimate the number of constraints based on the topological model for sodium boroaluminosilicate glasses⁴⁶ and the previous structural work on the lithium aluminoborate glass with $x = y = 0^{12}$. For this composition, it has been shown that the boron speciation is a mix of 83% B^{III} and 17% B^{IV} , while the aluminum speciation is a mix of 74% Al^{IV} , 23% Al^{V} , and 3% Al^{VI} . The structural changes in such silicoaluminoborate glasses is mostly dominated by the modifier-to-alumina ratio⁴⁷, and since this ratio is kept constant in all the present glasses, we assume the boron and aluminum speciation to be constant in the following estimation of the number of constraint (since no structural data are available for the present glasses). We note that this assumption

is not fully accurate, especially for the *y*-series glasses with Si-for-B substitution, but any variations are not expected to qualitatively influence the compositional trends in network rigidity. With these assumptions, we find that n_c increases with SiO₂ content in both series of glasses (Figure 3). The changes in network rigidity are generally small, but we find a larger increase in n_c for the *y*-series glasses with Si-for-B substitution. In recent work, properties such as hardness⁴⁸ and elastic moduli^{49,50} have been found to scale better with constraint density (n'), i.e., the number of constraints per volume. We compute n' based on n_c and the measured molar volume. n' also increases with increasing silica content, but the larger increase for the second glass series is even more pronounced for n' compared to that for n_c (Figure 3). We note that this increase in network rigidity upon silica addition is expected to improve the chemical durability of the aluminoborate glasses²², but it has not been measured in the present study.

3.3 Glass transition temperature

Figure 4 shows the compositional evolution of the glass transition temperature (T_g). We find that T_g is slightly positively correlated with the addition of SiO₂. As discussed above, the addition of SiO₂ results in a more rigid glass network, i.e., more atomic constraints per atom (higher connectivity), which has been shown in earlier work to be positively correlated with higher glass transition temperature⁵¹. In agreement with the relatively small changes in n_c with composition (Figure 3), the changes in T_g are small (up to ~10 K) compared to the large change in composition (20 mol%). Furthermore, we note that there is a larger apparent increase in T_g for the *x*-series of glasses where SiO₂ is introduced by scaling down the other components proportionally, despite its smaller estimated increase in n_c compared to the *y*-series of glasses. This is likely because the average bond energy increases more in the former, since weak Li-O bonds are replaced by stronger Si-O bonds.

3.4 Elasticity and hardness

Figure 5 shows the elastic moduli (E , G , B) and Poisson's ratio (ν) of the glasses with different extent of SiO₂ doping. As seen for glass transition temperature, the addition of SiO₂ has only a relatively small effect on the elastic moduli for the two series glasses. For the *x*-series glasses (Figure 5a), there

is either no change or a small decrease in elastic moduli with SiO₂ content. On the other hand, the *y*-series glasses exhibits a small increase in elastic moduli (Figure 5b). Elastic moduli generally increase with the bond strength and the number of bonds per volume⁵². Recent topological models have found *E* to be positively correlated with *n'*^{49,50}, which qualitatively agrees with the larger increase in *n'* for the *y*-series glasses with Si-for-B substitution (Figure 3). However, it cannot explain why there is a minor decrease in *E* with silica content for the *x*-series glasses (Figure 5a). According to the model in Ref.⁵⁰, this could only be possible if some linear-bond stretching constraints are transformed into angular-bond bending constraints, since the typical free energy for the former is larger than for the latter type of constraints. Additional structural characterization or atomistic simulations would be needed to confirm this.

The addition of SiO₂ also affects the Poisson's ratio for both series of glasses, although all glasses are within the relatively narrow range of 0.26 to 0.29. For the initial silica addition (2 to 10 mol%), Poisson's ratio for both series shows a negative correlation with the addition of SiO₂. This makes sense in terms of the compositional trend in *C_g* (Figure 2), since more open networks are generally found to feature more volume compared to shape change upon deformation and thus have lower Poisson's ratio⁵². However, when the silica addition increases to 20 mol%, the Poisson's ratio increases, especially for the *x*-series glasses. For this series, when the addition of silica reaches 20 mol%, Al₂O₃ and Li₂O are strongly diluted. Therefore, the probability of finding Li⁺ ions in proximity to aluminum species could be decreasing. It is thus possible that more lithium ions than the simple excess (i.e., [Li₂O]-[Al₂O₃]) act as modifiers instead of charge-compensating aluminum tetrahedra. Such structure changes should increase the extent of NBO formation, which makes the network more prone to shear, resulting in an increase in *v*.¹⁴

Figure 6 shows the composition dependence of Vickers hardness, which has been determined using the micro-indentation method. The addition of SiO₂ has a positive effect on the Vickers hardness for both series of glasses. As for elastic moduli, the results can be understood in terms of the changes in constraint density with composition, which has been proposed to scale with hardness⁴⁸. That is, hardness increases with silica content due to the concomitant increase in *n'*, which also

explains the larger observed increase in hardness for the *y*-series glasses with Si-for-B substitution (Figure 6). The hardness model of Zheng *et al.*⁴⁸ is given as,

$$H_V = (dH_V/dn') \cdot n',$$

(9)

where dH_V/dn' is a scaling factor. By setting $dH_V/dn' = 0.071 \text{ GPa nm}^3$, which is within the range of values reported previously⁴⁸, we obtain hardness values of 4.5, 4.6, and 4.8 GPa for the glasses with $x = y = 0$, $x = 20$, and $y = 20$, respectively. These model predictions (see dashed lines in Figure 6) are in good agreement with the experimental data in Figure 6.

3.5 Indentation deformation

Next, we consider the extent of densification during indentation to understand the cracking behavior of the glasses. Figure 7 shows optical micrographs of indents produced at 4 N on the surface of the glass $20\text{SiO}_2\text{-}35\text{B}_2\text{O}_3\text{-}25\text{Li}_2\text{O-}20\text{Al}_2\text{O}_3$ ($y = 20$) before and after annealing at $0.9T_g$ for 2 h. A significant deformation recovery zone is observed in the glass after annealing the indent. As shown in Figure S3 in the Supporting Information, there is an apparent recovery zone for both series of glasses after re-annealing at $0.9T_g$ for 2 h. However, the addition of SiO_2 does not cause noticeable differences in the extent of the deformation recovery zone.

The extent of indentation-induced densification is typically quantified from the ratio between the densification and the total indentation volumes, referred to as the volume recovery ratio (V_R)²³. Here, we use a similar metric, which we have found to scale well with V_R (unpublished data), namely the recovery of the indentation side length upon annealing (L_{SR}). Figure 8 shows the composition dependence of L_{SR} . It is clear that the addition of SiO_2 has a negligible effect on the side recovery of the indents in the glasses, which we interpret as a competition of two effects. On the one hand, B and Al atoms are removed due to the addition of SiO_2 , leading to less densification, since Si (unlike B and Al) does not readily change its coordination number as a result of the stresses created during indentation. On the other hand, C_g of the two series of glasses decreases with the increasing content of SiO_2 . More open glass networks could lead to more densification. Therefore, it is possible that these

two opposite effects cancel each other, resulting in constant densification contribution to indentation upon silica addition.

3.6 Indentation cracking

In the Vickers indentation test, crack initiation occurs under a sufficiently high load, and is attributed to the mismatch between the plastic deformation volume and the surrounding elastically-deformed material^{53,54}. Crack resistance (*CR*) is derived from the load leading to formation of two radial cracks per indent, which are the dominant crack-type in the investigated glasses. Figure S4 in the Supporting Information shows images of the radial cracks generated in the two glass-series. Figure 9 shows the composition dependence of *CR* of the two series of glasses. Different experiment conditions (such as relative humidity, loading rate, and surface quality) and slight composition variations can have a pronounced impact on the value of *CR*. Therefore, compared with the previous work,¹² the 55B₂O₃-25Li₂O-20Al₂O₃ ($x = y = 0$) glass in this study has a slightly lower *CR* value than that previously reported. Furthermore, the addition of SiO₂ has a significant effect on the *CR* for both series, i.e., *CR* decreases with the silica content. Building on our recent work¹² showing that the coordination number changes during indentation (termed self-adaptivity) are more important for *CR* than packing density, the observed decrease in *CR* is due to the removal of Al₂O₃ and/or B₂O₃ with the addition of SiO₂. This compositional changes makes the network less structurally-adaptive to applied stress, although the silica-containing networks have more free volume. However, they cannot densify more during densification (Figure 8), and this leads to an overall decrease in crack resistance upon SiO₂ addition. Finally, we note that besides the overall decrease in *CR* with silica addition, there is a local minimum in *CR* for both the glasses with $x = 2$ and $y = 2$. The structural origin of this apparent minimum is unknown.

4. Conclusions

We have studied the structure and mechanical properties of two series $\text{SiO}_2\text{-B}_2\text{O}_3\text{-Li}_2\text{O-Al}_2\text{O}_3$ glasses with varying addition of SiO_2 . By using micro-Raman spectroscopy, we have found that the addition of SiO_2 partially disturbs the borate network, thus increases the average network rigidity but decreasing the atomic packing density, i.e., that the network becomes gradually more open and rigid with silica addition. By using a previous constraint hardness model, we are able to quantitatively account for the composition dependence of hardness of based on the competing effects of free volume and network rigidity. The removal of B and Al atoms due to the addition of SiO_2 should lead to less structural densification (i.e., involving changes in coordination numbers), whereas the more open glass networks should lead to more densification (i.e., at constant coordination numbers). As a result, there is no apparent effect of silica addition on the side recovery of the indents, i.e., on the indentation deformation mechanism. In agreement with our recent work showing that the coordination number changes during indentation (termed self-adaptivity) are more important for crack resistance than packing density, we find that the addition of SiO_2 leads to an overall decrease in crack resistance. In other words, the addition of SiO_2 does not necessarily lead to a pronounced increase in physical properties, although pure SiO_2 has high glass transition temperature, hardness, and crack resistance. As shown and discussed in this work, it is due to the complex structural interactions in mixed network former glasses and the competitive effects of free volume and network rigidity.

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FIGURE CAPTIONS

Figure 1. Micro-Raman spectra of the two series of lithium silicoaluminoborate glasses with different content of SiO₂. The spectra are divided into five different band regions. (a) *x*-series. (b) *y*-series.

Figure 2. Composition dependence of density (ρ), molar volume (V_m) and atomic packing density (C_g) for the two series of lithium silicoaluminoborate glasses. The errors in ρ , V_m , and C_g do not exceed 0.002 g/cm³, 0.02 cm³/mol, and 0.001, respectively.

Figure 3. Composition dependence of n_c (number of constraints per atom) and n' (number of constraints per volume) for the two series of lithium silicoaluminoborate glasses.

Figure 4. Composition dependence of the glass transition temperature (T_g) for the two series of lithium silicoaluminoborate glasses. The error in T_g does not exceed 2 °C.

Figure 5. Composition dependence of elastic moduli (Young's (E), shear (G), bulk (B)) and Poisson's ratio (ν) for the two series of lithium silicoaluminoborate glasses. The errors in E , G , B , and ν do not exceed 2 GPa, 1 GPa, 1 GPa, and 0.005, respectively. (a) *x*-series. (b) *y*-series.

Figure 6. Composition dependence of indentation hardness for the two series of lithium silicoaluminoborate glasses. The dashed lines represent the model predictions using Eq. (9) with $dH_V/dn' = 0.071$ GPa nm³.

Figure 7. Optical micrographs of indents produced at 4 N on the surface of the glass (20SiO₂-35B₂O₃-25Li₂O-20Al₂O₃) before and after re-annealing at $0.9T_g$ for 2 h.

Figure 8. Composition dependence of indentation side recovery (L_{SR}) for the two series of lithium silicoaluminoborate glasses.

Figure 9. Composition dependence of the crack resistance (CR) for the two series of lithium silicoaluminoborate glasses. The estimated error in CR is 20% of its value.





















