Crack-resistant $\text{Al}_2\text{O}_3$–$\text{SiO}_2$ glasses

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Obtaining “hard” and “crack-resistant” glasses have always been of great importance in glass science and glass technology. However, in most commercial glasses both properties are not compatible. In this work, colorless and transparent $x\text{Al}_2\text{O}_3$–$(100-x)\text{SiO}_2$ glasses ($30 \leq x \leq 60$) were fabricated by the aerodynamic levitation technique. The elastic moduli and Vickers hardness monotonically increased with an increase in the atomic packing density as the $\text{Al}_2\text{O}_3$ content increased. Although a higher atomic packing density generally enhances crack formation in conventional oxide glasses, the indentation cracking resistance increased by approximately seven times with an increase in atomic packing density in binary $\text{Al}_2\text{O}_3$–$\text{SiO}_2$ glasses. In particular, the composition of $60\text{Al}_2\text{O}_3$–$40\text{SiO}_2$ glass, which is identical to that of mullite, has extraordinary high cracking resistance with high elastic moduli and Vickers hardness. The results indicate that there exist aluminosilicate compositions that can produce hard and damage-tolerant glasses.

Strong glasses combining the mechanical attributes of being “hard” and “crack-resistant” are required in many technological fields including construction, transportation, and electronics. However, the inherent brittleness of glasses limits their applications. The simultaneous realization of high hardness and crack resistance has always been an important issue in glass science and technology.

The hardness of glasses is often evaluated by Vickers hardness $H_v$, which is estimated from the size of indentation imprint. Vickers hardness in conventional oxide glasses can be predicted with relative good accuracy using compositional and structural parameters. Yamane et al. proposed an equation for silicate glasses in which $H_v$ is proportional to the square root of the product between the bulk modulus $K$, shear modulus $G$, and the average single-bond energy between the component cations and oxygen. Positive linear trends have been found between Vickers hardness and Young's modulus $E$. According to the Makishima and Mackenzie model, the Young's modulus $E$, bulk modulus $K$, and shear modulus $G$ of glasses are related to both the dissociation energy per unit volume of the components and the atomic packing density of the glass. In case of alkali–alkaline earth silicate glasses, it was found that glasses with more packed structures had higher values of hardness and the elastic modulus. $\text{Al}_2\text{O}_3$–$\text{R}_2\text{O}$ and $\text{Al}_2\text{O}_3$–$\text{SiO}_2$–$\text{R}_2\text{O}$ glasses ($\text{R} = \text{Y}, \text{Sc}, \text{or} \text{Ta}$) are among the hardest oxide glasses ($H_v$ up to 9.5 GPa) with high elastic moduli ($E$ up to 169 GPa). This is attributed to their high atomic packing density and high dissociation energy unit volume of components. Based on successful theoretical temperature-dependent constraints, a recent model was proposed in which $H_v$ is proportional to the number of bond-stretching and bond-bending constraints at room temperature in oxide glasses. These results suggest that a hard glass with high elastic moduli require a high atomic packing density and high bonding energy of components.

“Crack-resistant” or low–brittleness glasses should be resistant to surface damage or fracture. An effective way to increase the cracking resistance of glasses is chemical or physical strengthening of the glass surface by creating a compressive stress layer at the surface that prevents crack initiation and propagation. The thickness of the compressive stress layer is limited to a few microns beneath the surface without affecting the interior physical properties of the glass. Low–brittleness glasses have been designed by adjusting the chemical composition to enhance the glass deformation ability. Sehgal and Ito developed a less-brittle (LB) soda–lime–silica glass with remarkably high indentation cracking resistance by tuning the molar volume of the glass. Also, Sehgal and Ito showed that the LB glass displayed a lower brittleness and higher indentation fracture toughness than normal soda-lime silicate glass. Gross et al. synthesized a $10\text{CaO}\cdot10\text{Al}_2\text{O}_3\cdot80\text{SiO}_2$ glass with high-crack initiation load and fictive temperature-independent elastic modulus. Morozumi et al. fabricated a sodium aluminoborosilicate glass with a high intrinsic cracking-initiation load. These crack-resistant glasses can release the stress without cracking by atom displacements, resulting in plastic deformation mainly by densification and, to a certain extent, by shear deformation. Because of their high molar volume and low atomic packing density, in these glasses atoms can easily be compacted by force. Moreover, crack-resistant glasses are characterized for having low elastic moduli and Vickers hardness ($H_v$ approximately 5–6 GPa and $E$ approximately 60–70 GPa). Therefore, it is

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accepted that “hard” and “crack-resistant” are not achieved simultaneously in conventional oxide glasses because high packing density is a characteristic of hard glasses. On the contrary, in this paper, we show that alumina-rich Al₂O₃–SiO₂ binary glasses exhibit both high hardness and cracking resistance. Furthermore, we investigated the correlation among atomic packing density, elastic moduli, and indentation of the binary aluminosilicate glasses.

### Results

The Al₂O₃–SiO₂ binary glass system is important in geosciences, glass-ceramics, and is a base composition for fabricating multiple commercial glasses. It has been widely studied owing to its interesting structure and phase-separation phenomena. In particular, binary aluminosilicate glasses with more than 30 mol% of Al₂O₃ are difficult to fabricate in the bulk form by conventional melting processes because of their low glass-forming ability and high melting temperatures. Al₂O₃-rich glasses have been prepared by splat quenching, flame spraying, roller quenching, sol-gel, and containerless processing. Most techniques produce thin flakes or small particles, whereas containerless processing has the advantage of producing bulk glasses by solidification without heterogeneous nucleation at the surface of the melt. Recently, it has been reported that TiO₂-, Nb₂O₅-, WO₃-, and Al₂O₃-based glasses without any network formers have been successfully fabricated with this method. Weber et al. obtained Al₂O₃–SiO₂ glasses with Al₂O₃ content up to 67 mol% by aerodynamic levitation (ADL); however, the diameter of the glass samples was at most 1 mm. In this work, we used the ADL technique for fabricating bulk Al₂O₃–SiO₂ glasses with high alumina content.

Transparent and colorless xAl₂O₃–(100–x)SiO₂ glasses were obtained in the range of 30 ≤ x ≤ 60. At x ≥ 60, mullite and α-Al₂O₃ directly crystallized from a melt. The properties of the glasses are summarized in Table 1. Figure 1A shows the composition dependence of density ρ and atomic packing density Cₚ. Both ρ and Cₚ increase linearly with Al₂O₃ content and are in good agreement with the previous results obtained from roller-quenched and splat-quenched amorphous flakes. The glasses become more packed and rigid as alumina content increases. Figure 1B shows that all the elastic moduli increase linearly with x. Young’s modulus E increases from 102.9 GPa to 134.2 GPa, bulk modulus K increases from 65.6 to 99.0 GPa, shear modulus G increases from 41.5 GPa to 52.7 GPa, and Poisson’s ratio ν increases from 0.239 to 0.274 with increasing alumina content. The values of ρ, Cₚ, and E seem to extrapolate linearly to the pure SiO₂ composition. In Fig. 1C, the Vickers hardness Hᵥ increases monotonically with increasing Al₂O₃ content from 7.23 to 8.07 GPa in agreement with the elastic moduli trends. The increase in elastic moduli and hardness of xAl₂O₃–(100–x)SiO₂ glasses with increasing x follows the expected relation between elastic moduli and hardness as well as the atomic packing density and dissociation energy per unit volume of the components. The increase in Al₂O₃ content enhances the atomic packing density and total dissociation energy of the glass because of the large dissociation energy of Al₂O₃ per unit volume (Gₐl₂o₃ = 131 kJ/cm³) compared with SiO₂ (Gₛiₒ₂ = 68 kJ/cm³). As a result, the glass with the highest Al₂O₃ content (x = 60) with mullite composition shows the highest elastic moduli and Vickers hardness. These values are comparable to hard glasses, such as R₂O₃–SiO₂–Al₂O₃ or CaO–SiO₂–Al₂O₃ glasses, and are much larger than those of crack-resistant silicate or borosilicate glasses.

In order to rule out any surface effect in the glasses obtained by the levitation system we compared the hardness and indentation imprints of pure SiO₂ glass as prepared by the aerodynamic levitation system with a reference SiO₂ glass (Edmund optics). The values of indentation hardness Hᵥ were 8.69 ± 0.08 GPa and 8.69 ± 0.07 GPa for the levitation SiO₂ glass and the reference SiO₂ glass respectively. Also, the indentation imprints displayed the same cracking patterns with cone cracks typical of anomalous glasses and similar cracking frequency. These results suggest that there is no apparent surface effect on the indentations properties of the glasses obtained through the levitation system. Figure 2 shows the Vickers imprints on xAl₂O₃–(100–x)SiO₂ glasses for various loads. It is noted that with increasing Al₂O₃ content, the glasses become more resistant to radial cracking (observed at the imprint corners) although the atomic packing density increased. Normal (radial cracks) behavior is observed in all samples for x = 30, 40, 45, 50, and 55 and, whereas no cracks were observed in more than 50% of the indentation imprints for glasses with x = 60 even using an indentation load of 49.03 N. To quantify the resistance to fracturing, cracking probability curves are shown in Fig. 3. The data were fitted by using a sigmoid function. From the fitting curve, the loading force required to generate a 50% cracking probability or 2 radial cracks in average (cracking resistance CR) was estimated. As shown in the inset, CR increases drastically at x ≥ 50. The CR value of 55.4 N for the x = 60 glass is considerably larger than those of the crack-resistant glasses.

### Table 1. Density ρ, atomic packing density Cₚ, sound velocities, elastic moduli, and indentation properties of xAl₂O₃–(100–x)SiO₂ glasses including pure SiO₂ glass.

| x   | ρ (g/cm³) | Cₚ | V₁ (km/s) | V₂ (km/s) | L (GPa) | E (GPa) | K (GPa) | G (GPa) | ν | Hᵥ (GPa) | CR (N) |
|-----|-----------|----|-----------|-----------|---------|---------|---------|---------|---|----------|--------|
| 0   | 2.21      | 0.456 | 6.06     | 3.75      | 81.2    | 73.9    | 39.7    | 31.1    | 0.190 | nd       | nd     |
| 30  | 2.55      | 0.506 | 6.89     | 4.04      | 121.0   | 102.9   | 65.6    | 41.5    | 0.239 | 7.23     | 7.8    |
| 40  | 2.65      | 0.518 | 7.13     | 4.12      | 134.4   | 112.3   | 74.4    | 45.0    | 0.248 | 7.50     | 5.5    |
| 45  | 2.68      | 0.522 | 7.27     | 4.17      | 141.7   | 117.1   | 79.5    | 46.7    | 0.254 | 7.70     | 9.1    |
| 50  | 2.74      | 0.531 | 7.41     | 4.22      | 150.5   | 122.8   | 85.6    | 48.7    | 0.261 | 7.79     | 13.4   |
| 55  | 2.79      | 0.539 | 7.58     | 4.29      | 160.6   | 129.9   | 92.1    | 51.3    | 0.265 | 7.92     | 19.8   |
| 60  | 2.85      | 0.546 | 7.71     | 4.30      | 169.2   | 134.2   | 99.0    | 52.7    | 0.274 | 8.07     | 55.4   |
(N₂), a 80SiO₂•10Al₂O₃•10CaO glass had CR of approximately 10 N under N₂, an aluminoborosilicate commercial glass had CR of 11 N at 30% relative humidity, and a 80SiO₂•15Na₂O•5CaO glass had 10 N CR at 30% relative humidity¹⁸,¹⁹,²²,⁴¹. It is well known that the indentation cracking resistance in silicate glasses strongly depends on the atmosphere during measurements and that humidity decreases CR⁴²,⁴³. Therefore, it is likely that the CR of the x = 60 glass will increase when measured in a nitrogen atmosphere. The large CR of the x = 60 glass is comparable to chemically strengthened soda lime glass¹⁷.

**Discussion**

Oxide glasses with large CR usually have enough free space to dissipate the mechanical stress owing to densification (compaction) and to lesser extent shear deformation. Therefore, large CR in oxide glasses should correlate to open structure (less-packed)¹⁸,²¹,²²,²⁵. Rouxel et al. suggested the use of Poisson’s ratio ν as to describe the available free volume in glasses⁴⁴. Based on hydrostatic compression experiments, the simple equation Δρ/ρ₀ = 150 exp(−13ν) was proposed, where Δρ/ρ₀ is the maximum relative density change, ρ₀ is the initial density, and Δρ is the density change owing to hydrostatic stress⁴⁴. In case of xAl₂O₃–(100–x)SiO₂ glasses, the Δρ/ρ₀ decreases from 6.71% to 4.25% with increasing x from 30 to 60. This suggests that increasing the Al₂O₃ content may reduce the ability for densification therefore decreasing the cracking resistance. Moreover, Sellapan et al. showed that the radial/median cracking ability of silicate and borosilicate glasses may be classified in relation to their Poisson’s ratio ν as: resistant 0.15 ≤ ν ≤ 0.20, semi-resistant 0.20 ≤ ν ≤ 0.25, and easily damaged 0.25 ≤ ν ≤ 0.30⁵². Based on Poisson’s

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**Figure 1.** Composition dependence of (A) the density ρ and the atomic packing density Cₚ, (B) elastic moduli: L (C₁₁), K, G (C₄₄), E and ν, and (C) Vickers hardness Hv for the xAl₂O₃–(100–x)SiO₂ glasses. The data for SiO₂ glass are shown at x = 0.
ratio, the Al2O3–SiO2 glasses should change from semi-resistant to easily damaged as the Al2O3 content increases. However, it is observed that CR increases with alumina content. The increase in the CR of binary aluminosilicate glasses is the opposite of what is expected. Apparently, other mechanism to prevent crack initiation should be taken in consideration.

Shear deformation is an alternative mechanism in conventional oxide glasses. In oxide glasses, such deformation likely occurs in the vicinity of atoms that are weakly bonded owing to the existence of non-bridging oxygen, as observed in sodium silicate glasses. In case of binary Al2O3–SiO2 glasses, non-bridging oxygens were not confirmed by XPS measurements. Thus, shear deformation owing to the movement of non-bridging oxygens is rather unlikely. Shear deformation will also occur in borate glasses where easy-slip units such as boroxol rings exist or where BO3–BO4 species exchange occurs under applied stress. Recently, similar shear deformation processes have been proposed to occur in densified silica glass. As in the case of BO3 and BO4 units in borate glasses or SiO4, SiO5 and SiO6 units found by molecular dynamics in densified silica glass, different structural units, such as AlO4, AlO5, and AlO6 have been observed in Al2O3–SiO2 glasses. 27Al Magic Angle Spin (MAS) NMR and molecular dynamics (MD) simulations have shown that alumina-rich Al2O3–SiO2 glasses contain high quantities of distorted AlO4 species (about 30–49% of Al sites) apart from AlO4 and AlO6.

Figure 2. Vickers indentation imprints for the xAl2O3–(100–x)SiO2 glasses. Blue-shaded photographs show the cracked samples. Gray-shaded photographs show the non-cracked samples. Each indentation imprint represents more than 50% of the indentations.

Figure 3. Cracking probability curves for the xAl2O3–(100–x)SiO2 glasses. The inset shows the composition dependence of the cracking resistance.
based on oxygen diffusion in melts, it was suggested that AlO3 units in Al2O3–SiO2 glasses are trapped in the glass structure in a meta-stable state between the AlO3 in liquids and AlO3 in crystalline materials like mullite33,34. In this sense, it is probable that the multiple coordination environments of Al atoms as well as the mid-range structure around these units play a role on the enhancement of the cracking resistance through shear deformation processes. Although the overall mechanism is still not clear it is important to note that shear deformation processes are favored as the packing density and Poisson’s ratio increases which is observed in the studied system as the alumina content increases. Accordingly, there is a possibility that plastic deformation may be aided not only by densification but also by shear deformation processes in Al2O3–SiO2 glasses.

Conclusion
The elastic properties and indentation of xAl2O3-(100–x)SiO2 glasses prepared by aerodynamic levitation were investigated. All glasses in the range 30 ≤ x ≤ 60 were colorless and transparent. The elastic moduli and hardness increased monotonically with alumina content from x = 30 to x = 60. The steady increase of the elastic moduli and hardness can be explained by the increasing atomic packing density and the high dissociation energy per unit volume of Al2O3 compared to SiO2. Furthermore, it was found from the indentation imprints that the glass cracking resistance increases with increasing alumina. As a result, alumina-rich Al2O3–SiO2 glasses are strong materials because of their high hardness and high indentation cracking resistance. In particular, the 60Al2O3•40SiO2 glass displayed the highest indentation cracking resistance, elastic moduli, and hardness in the binary system. The increase in cracking resistance cannot be explained only by densification as it is widely accepted for conventional oxide glasses. Thus, it is proposed that the local structure of aluminum atoms as well as the structure around these units may play a role in the increased cracking resistance of alumina-rich Al2O3–SiO2 glasses through shear deformation processes.

Methods
Glass synthesis. The glasses were fabricated using an aerodynamic levitation furnace described elsewhere22. Alumina (α-Al2O3) and SiO2 powders (99.99% purity) were mixed in stoichiometric proportions of xAl2O3–(100–x)SiO2 with x = 30, 40, 45, 50, 55, 60. The mixed powders were pelletized in a hydrostatic press and then heated in air at 1050 °C for 12 h. Pieces of the crushed pellets were melted at temperatures between 1800 °C and 2000 °C using two CO2 lasers in an ADL furnace. Oxygen was used for levitating the melt and for avoiding SiO2 evaporation. The levitated melts were solidified by turning off the lasers at a cooling rate of a few hundreds of degrees per second. The diameter of the solidified samples was approximately 2 mm. Glass formation was confirmed by Cu Kα XRD (Rigaku, RINT 2000). Fused silica glass (T-4040, Covalent Materials Corp.) was used for reference.

Density and atomic packing density. The density ρ of the glasses was determined using gas pycnometry (Micromeritics, AccuPycII 1340). The atomic packing density Cp was calculated from the experimental density using the formula Cp = ρΣ(xiVi)/M, where M is the molecular mass of the glass, xi is the molar fraction of oxide i, and Vi is the ionic volume of oxide i. The ionic volume is given by Vi = Nₐ(4/3)π(aᵣᵢ³ + rᵢ³), where Nₐ is Avogadro’s number, m is the number of atoms in the AₘOₙ oxides, rᵢ is the ionic radius of the cation, and rᵢ is the ionic radius of oxygen. The coordination number of Al³⁺, Si⁴⁺, and O²⁻ was assumed 4, 4, and 2, respectively. Shannon and Prewitt ionic radii were used23.

Elastic moduli measurement. The pulse-echo overlap technique was used to obtain the sound velocities of the glass24. A 50 μm thick ultrasonic transducer (LiNbO3 10° Y-cut) and a 500-μm thick glass were pasted at opposite corners of a corner-trunced tungsten carbide (WC) block using a conductive epoxy resin. The ultrasonic echoes of the longitudinal (L) and shear (T) waves from the transducer were reflected by the glass and observed using a digital oscilloscope. The longitudinal velocity Vₓ and transversal velocity Vᵧ were determined by dividing the thickness of the samples by the observed travel time of the waves. The longitudinal modulus L (Ciₓ), and shear modulus G (Ciᵧ) were estimated using equations L = ρVₓ² and G = ρVᵧ². The Young’s modulus E, bulk modulus K, and Poisson’s ratio ν were calculated using equations E = G(3L – 4G)/(L – G), K = L – (4/3)G, and ν = (L – 2G)/(2L – 2G), respectively. The elastic properties of SiO2 glass were also measured for comparison.

Indentation behavior. In order to rule out any surface effect in the glasses obtained by the levitation system we compared the hardness and indentation imprints of pure SiO2 glass as prepared by the aerodynamic levitation system with a reference SiO2 glass (Edmund optics). Spherical SiO2 samples obtained by aerodynamic levitation were mirror-polished into a disk shape with a thickness of 500-μm. The indentation experiments were made using a dynamic indenter (Shimadzu DUH-211) loaded with a diamond Berkovich 115° indenter in an atmosphere with 60% relative humidity. The loading and unloading rate was set to 70.067 mN/s using a dwell time of 15 s. The indentation hardness was calculated from the equation Hᵥ = Fᵥmax/Aᵥp, where Fᵥmax is the applied load and Aᵥp = ρ₀h₀ = 0.75(bᵥmax – hᵥ) is the projected contact area, where bᵥmax is the maximum penetration at Fᵥmax and hᵥ is the point of intersection between the tangent of the linear section of the unloading curve and the indentation depth axis. Ten indentations were performed for each SiO2 glass sample. The resulting imprints were observed by optical microscopy. For the Al2O3–SiO2 glasses indentation experiments were performed using a Vickers hardness tester at 23 °C and 60% relative humidity. Mirror-polished glasses with approximately 500-μm thickness were used. A Shimadzu DUH HMV-1 Vickers tester and an Akashi AVK-C2 Vickers tester were used for indentation loads below 19.6 N and over 19.6 N, respectively. The dwell time was 15 s. Vickers hardness HV was calculated from the diagonal length of the imprints at a load of 4.903 N. To evaluate the cracking resistance CR to radial cracks, the number of corners (four) divided the number of cracks for each indentation and the results were averaged by the number of indentation tests. The averaged value is the cracking probability at specific load. Cracking probability curves were obtained by plotting the cracking probability as a function of the loading force.
The indentation cracking resistance (CR) is defined as the load required for generating two radial/median cracks on average or associated with 50% cracking probability. Three specimens were used for each composition. At least 20 indentation imprints were used to calculate the $H_v$ and CR at each load.

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**Author Contributions**

G.A.R.S. wrote the manuscript, analyzed the results, fabricated the glasses and conducted the indentation experiments, A.M. wrote the manuscript, organized the research and analyzed the results, Y.H. conducted the elastic moduli measurement, and H.I. analyzed the results and organized the research. All authors reviewed the manuscript.

**Additional Information**

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