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Structural origin of high crack resistance in sodium aluminoborate glasses

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ABSTRACT

Sodium aluminoborate glasses are found to exhibit favorable mechanical properties, especially high crack resistance, due to their relatively low resistance to network compaction during sharp-contact loading. We here reveal the origin of the high crack resistance by investigating changes in structure and mechanical properties in compositions ranging from peralkaline to peraluminous and by varying the pressure history through an isostatic N_2-mediated pressure treatment at elevated temperature. This approach allows us to study the composition dependence of the ease of the glassy network compaction and the accompanying changes in structure and properties, which shed light on the processes occurring during indentation. Through solid state NMR measurements, we show that the network densification involves an increase in the average coordination number of both boron and aluminum and a shortening of the sodium-oxygen bond length. These changes in the short-range order of the glassy networks manifest themselves as an increase in, e.g., density and indentation hardness. We also demonstrate that the glasses most prone to network compaction exhibit the highest damage resistance, but surprisingly the crack resistance scales better with the relative density increase achieved by the hot compression treatment rather than with the extent of densification induced by indentation. This suggests that tuning the network structure may lead to the development of more damage resistant glasses, thus addressing the main drawback of this class of materials.

1. Introduction

Glassy solids offer a range of favorable properties such as transparency, high hardness, relatively light-weight, low-cost raw materials, and in many cases excellent chemical resistance, making them desirable materials for many traditional and novel applications [1]. However, their brittleness, low practical strength, and limited toughness are major drawbacks for future applications, although various post-treatment methods such as thermal [2] and chemical strengthening [3] are being applied to improve the glass mechanics. In addition, significant contributions to improving the mechanical performance through tuning of the chemical composition have been made [4–7], but a fundamental understanding of the composition dependence of crack initiation and growth in glasses is still lacking.

In 1921, Griffith [8] suggested that the low practical strength of oxide glasses is due to surface flaws as stresses concentrate at the tips of the flaws leading to a brittle fracture considering that such glasses do not have a stable shearing mechanism. Sharp-contact loading (i.e., indentation) has subsequently been employed to introduce surface flaws in a controlled manner and to observe the cracking patterns originating from the residual indentation imprint [9–14]. Examination of considerable amounts of indents lead to the observation that different glass systems deform via different mechanisms, which in turn dictate the crack resistance and pattern. Glasses which densify upon indentation tend to form ring cracks around an indent, whereas glasses deforming through volume-conservative shear flow are more likely to form radial/median cracks propagating outwards from the corners of an indent [12]. Later studies quantified the relative contributions of these deformation mechanisms and suggested that the deformation behavior (and thereby the type of cracking) is correlated to the atomic packing density (C_g) and in turn Poisson's ratio (ν) [15–18]. However, knowledge of the compositional scaling of the indentation crack

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resistance (*CR*) and its relation with other material properties is more limited.

The link between chemical composition and glass network structure, which in turn affects material properties and cracking behavior of a glass, has been thoroughly investigated, especially given the advances in structural characterization techniques, such as solid state nuclear magnetic resonance (NMR) spectroscopy and neutron diffraction. For example, the network of amorphous silica consists of corner-sharing SiO_4 tetrahedra [19,20], resulting in a low C_g value that favors densification during indentation [15,21]. Addition of modifier oxides (e.g., Na_2O) to the silicate network tends to fill the interstices with cations and induce the formation of non-bridging oxygens (NBOs), thus hindering densification and facilitating shear flow [22]. These structural changes strongly affect *CR* [16,17]. On the other hand, it has been shown in alkali borate glasses that the resistance to densification is unaffected by the increase in C_g upon alkali oxide addition [23]. This demonstrates that further studies are required in order to completely understand the role of chemical composition in governing the deformation and cracking behavior in oxide glasses.

In the search for more damage resistant glass compositions, we here consider a series of sodium aluminoborate glasses, specifically $25Na_2O$-xAl_2O_3-$(75\text{-}x)B_2O_3$ with x varying between 5 and 30 mol%. The structure of alkali aluminoborate glasses has previously been investigated in Refs [24–29]. Through magic angle spinning (MAS) NMR studies on ^{11}B and ^{27}Al nuclei, it has been found that both of the network-forming tetrahedral species tend to compete for the charge-balancing Na-cations. There is a preference towards charge-balancing aluminum tetrahedra (Al^{IV}) rather than boron tetrahedra (B^{IV}). Hence, upon substitution of Al_2O_3 for B_2O_3, the fraction of four-fold coordinated boron species (N_4) decreases as Na-cations are being re-associated to supply the deficient positive charge to Al^{IV} units. As the molar content of Al_2O_3 exceeds that of Na_2O, five- and six-fold coordinated aluminum species (Al^{V} and Al^{VI}) are detected. The glasses in this selected system are thus expected to exhibit large differences in boron and aluminum speciation across the series, and also contain low levels of NBOs, given the needs of sodium cations to charge-stabilize boron and aluminum in tetrahedral configuration. The earlier studies did not examine the relation of aluminoborate structure to the mechanical properties, but low NBO content and low N_4 has previously been found to favor densification during indentation, which in turn should promote high values of *CR* [16,17]. As such, the sodium aluminoborate glasses are an ideal model system for revealing the structural origin of high crack resistance in oxide glasses.

In detail, we here examine the impact of glass structure on deformation mechanisms and cracking behavior through density, differential scanning calorimetry (DSC), solid state ^{11}B, ^{23}Na, and ^{27}Al NMR spectroscopy, and nano- and micro-indentation measurements. The contributions of densification and shear flow to indentation are determined using atomic force microscopy (AFM). Furthermore, we employ a N_2-mediated isostatic compression treatment carried out around the glass transition temperature (T_g) to tune the pressure history of the glasses. Compression of glasses at T_g is especially useful, since significant permanent volume increase can be obtained on large specimens (~cm^3), thus enabling the evaluation of the change in mechanical properties. Ultimately, insight into the origin of pressure-induced changes in the glassy network may improve the understanding of changes induced by external loading, such as indentation.

2. Experimental section

2.1. Sample preparation

Seven glass compositions in the system $25Na_2O$-xAl_2O_3-$(75\text{-}x)B_2O_3$ with $x = 5$, 10, 15, 20, 25, 27.5, and 30 mol% were prepared, thus covering both peralkaline and peraluminous compositions. To do so, Na_2CO_3, Al_2O_3, and H_3BO_3 powders were first mixed according to the target compositions and these mixtures were melted in Pt-Rh crucibles at 1200–1650 °C depending on the composition. The melts were quenched onto a steel plate and transferred into an annealing furnace at an estimated glass transition temperature (T_g) using SciGlass database [30]. The chemical compositions were measured using flame emission and inductively coupled plasma spectroscopy methods and results are given in Table 1. The samples are named according to the analyzed compositions (see Table 1).

The T_g values were determined from DSC measurements (DSC 449C, Netzsch) as the intercept between the tangent to the inflection point and the extrapolated isobaric heat capacity (C_p) value of the glass for a glass specimen with a known thermal history (i.e., preceded by cooling at 10 K/min). The C_p,T curves were acquired after calibrating the DSC output against a similar scan for a sapphire specimen. Glasses were then reannealed for 1 h at the respective T_g value, followed by a cooling in the order of 3 K/min achieved by turning off the annealing furnace. The amorphous nature of the glasses was confirmed by means of X-ray diffraction (Empyrean XRD, PANalytical).

All glass compositions were subjected to an isostatic N_2-mediated compression treatment at 1.0 GPa at their respective T_g value. The permanent compression of the glass samples was achieved by maintaining the high pressure and high temperature conditions for 30 min, and subsequent quenching with an initial 60 K/min cooling rate to room temperature. The pressure chamber was then decompressed at a 30 MPa/min rate. More details regarding the compression treatment setup can be found in Ref. [31].

2.2. Density

Density values of the as-prepared and compressed glasses were determined using the Archimedes' principle of buoyancy. The weight of each glass specimen (at least 1 g) was weighed in air and in ethanol ten times.

2.3. MAS NMR spectroscopy

^{11}B, ^{23}Na, and ^{27}Al MAS NMR spectra were acquired with commercial spectrometers (VNMRs, Agilent) and MAS NMR probes (Agilent) for four selected compositions (NAB-5, NAB-15, NAB-24 and NAB-30) and their compressed analogues. The samples were powdered in an agate mortar, packed into 3.2 mm zirconia rotors, and spun at 20 kHz for ^{11}B MAS NMR and 22 kHz for both ^{27}Al and ^{23}Na MAS NMR experiments. ^{27}Al and ^{23}Na MAS NMR data were collected at 16.4 T (182.34 and 185.10 MHz resonance frequencies, respectively), using a 0.6 μs (~π/12 tip angle) pulse width for uniform excitation of the resonances. A range of 400 to 1000 acquisitions were co-added and the recycle delay between scans was 2 s. ^{11}B MAS NMR experiments were conducted at 11.7 T (160.34 MHz resonance frequency), incorporating a 4 s recycle delay, short rf pulses (0.6 μs) corresponding to a π/12 tip angle, and signal averaging of 400 to 1000 scans. The acquired spectra were processed with minimal apodization and then referenced to aqueous boric acid (19.6 ppm), aqueous NaCl (0 ppm), and aqueous aluminum nitrate

Table 1
Analyzed chemical compositions, glass transition temperature (T_g), density (ρ), atomic packing fraction (C_g), and plastic compressibility (β) of the as-prepared sodium aluminoborate glasses. The errors in T_g, ρ, C_g, and β do not exceed ±2 °C, ±0.001 g/cm^3, ±0.001, and ±0.002 GPa^{-1}, respectively.

Glass-ID	$[Na_2O]$ (mol%)	$[Al_2O_3]$ (mol%)	$[B_2O_3]$ (mol%)	T_g (°C)	ρ (g cm^{-3})	C_g (−)	β (GPa^{-1})
NAB-5	25.7	5.0	69.3	474	2.257	0.548	0.044
NAB-10	25.2	10.3	64.5	468	2.244	0.534	0.049
NAB-15	25.2	15.3	59.5	455	2.242	0.522	0.051
NAB-20	25.5	20.4	54.1	451	2.240	0.510	0.061
NAB-24	25.5	24.4	50.1	446	2.253	0.502	0.062
NAB-28	25.2	28.0	46.7	458	2.273	0.502	0.061
NAB-30	25.0	30.2	44.8	470	2.290	0.502	0.062