



Composition and cooling-rate dependence of plastic deformation, densification, and cracking in sodium borosilicate glasses during pyramidal indentation



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ABSTRACT

Plastic deformation, densification, and cracking of sodium borosilicate (NBS) glasses were examined during indentation with a three-sided pyramidal indenter. Compositions of 74.0SiO₂–10.0B₂O₃–16.0Na₂O (NBS1), and 74.0SiO₂–20.7B₂O₃–4.3Na₂O–1.0Al₂O₃ (NBS2) (mol%) were investigated. The effect of thermal history was additionally considered for the NBS2 composition, which lies near the boron anomaly line. Hardness, elastic modulus, and fracture toughness were estimated with instrumented indentation techniques. Atomic force microscopy (AFM), Raman micro-spectroscopy, and post-indent annealing experiments were used to analyze surface topographies, densification, and recovery of deformed material. The results indicate that NBS1 exhibits a greater hardness and elastic modulus, and undergoes less densification than the NBS2 glasses. Different casting conditions influenced the plastic deformation and onset of crack initiation in NBS2. Interpretation of fracture toughness measured by indentation is complicated by residual stresses, densification during contact, and model assumptions. However, distinct differences in elastic modulus, plastic deformation and cracking between the glasses were noticeable. Such results and observations are discussed in terms of structural changes in the glass.

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1. Introduction

Instrumented indentation testing provides a means of examining elastic–plastic deformation behavior in materials where more conventional testing may not be feasible. In particular, it enables local probing of small volumes and, hence, correlation of mechanical response with local structure. This has generated significant interest for the study of deformation processes in macroscopically brittle glasses. While the mechanical strength of glasses (and other brittle materials) is inherently dominated by the surface properties of the material, i.e., the number and size of surface defects, it has been noted semi-empirically that the probability of local failure can be tailored by variations in chemical composition [1]. The notion of “defect resistance” has been introduced as a means to describe the glass' response to a sharp contact, which may result in material compaction or indentation cracking. Any means to reduce the probability of indentation cracking and/or to control the fracture pattern which is induced through indentation would pave the way toward glasses with significantly improved resistance to surface defects [2]. In this context, sodium borosilicate (NBS) glasses represent an especially interesting class of glasses. On the one side, they constitute a key group of glasses for specialty applications such as in lighting,

electronic devices, biomedical substrates and containers, as well as laboratory ware or display screens [3,4]. On the other side, due to their thermomechanical properties, their mechanical performance cannot readily be improved through conventional methods such as thermal or chemical toughening. However, as has recently been demonstrated for a series of model compositions, their local deformation and cracking behavior are particularly strongly dependent on the composition and, in particular, the presence of specific structural units, which provides a third lever for designing ultra-tough borosilicate-type glasses [5].

Here, we focus on two specific compositions from the alkali borosilicate ternary which represent archetypes of technologically relevant borosilicate glasses, referred-to as NBS1 and NBS2 in the following. We consider plasticity and fracture of these two glasses by studying their response to penetration by a three-sided pyramidal Berkovich indenter. In such an experiment, observations of elastic–plastic deformation can be made along with crack initiation and subsequent crack growth. As already noted, there are few other, if any, mechanical tests which provide such a broad view at the mechanical properties of a brittle material. However, the advantages offered by indentation testing also come with the disadvantage of a complex stress–strain environment where analytical solutions are only available under specific conditions. Measurements of elastic modulus, hardness, and, in the case of brittle solids, fracture toughness are also possible with instrumented indentation techniques, but often require models relating test data to material

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properties. That said, the combination of indentation observation and analyses with spectroscopic techniques (e.g., Raman spectroscopy), can provide descriptive insights regarding the relationship between constitutive behavior and local or molecular glass structure [6–8].

In an overly simplifying way, two modes of plastic deformation mechanisms have been distinguished during indentation of inorganic oxide glasses [9–12], namely, volume conservative plastic shear flow and structural densification. This differentiation has historically led to a classification according to deformation behavior into ‘normal’ and ‘anomalous’ glasses [13]. Here, normal behavior has been put into analogy with metal plasticity at low E/H ratio, i.e., low ratio between elastic modulus and hardness [14]. Anomalous behavior has been assigned to glasses showing evidence of densification beneath the contact. This argument arose from the well-known hydrostatic densification in amorphous solids as found in, e.g., diamond anvil cell experiments [15,16]. The degree of potential densification is governed by the molecular free volume of the respective glass composition and correlates with structural dimensionality and Poisson’s ratio [17]. It has, however, been noted that isostatic compaction is a much more complex process than simple congruent volume reduction. For example, in the case of borosilicate glasses, it is associated with reconstructive structural transitions and also with increasing elastic homogeneity, related to the inherent pressure-dependence of dynamic heterogeneity of super-cooled liquids [18–20]. Computational modeling of densification processes in constitutive relationships corresponds with observations of complex experimental conditions such as the Vickers hardness testing [21], which, in consequence, allows for such comparison of isostatic compression experiments and instrumented indentation.

In the classical viewpoint, fused silica and low-alkali borosilicate glasses have been shown to exhibit ‘anomalous’ behavior, while soda-lime glasses appear to show ‘normal’ behavior [5,8,10,13,22,23]. The differences between the two types of glasses are reflected in their physical properties (e.g., hardness), and in deformation in and around the contact (i.e., sink-in/pile-up of material at the contact periphery). Furthermore, influences of ‘anomalous’ behavior have been seen in deviations from expected indentation cracking behavior and it might be expected that densification of the material below the contact plays a strong role in crack initiation during indentation. However, the effects of permanent densification processes in glass on fracture toughness have yet to be explored in detail. While the above discussion focuses on continuum ideas of deformation/properties, the processes that control deformation during indentation are ultimately linked to the local glass structure which is a strong function of chemical composition and processing conditions [23]. Local molecular rearrangement and local network connectivity can be modified due to the intense contact pressures observed in indentation [7,8,24]. A more complex differentiation of potential deformation and compaction reactions has therefore been proposed recently [25], where compaction may be congruent (continuous) or, e.g., governed by structural transitions such as changes in atomic coordination. This picture is particularly important for the consideration of borosilicate glasses, in which the equilibrium between tetrahedral and trigonal borate-groups is known to strongly affect virtually all macroscopic properties. Not only changes in composition, but also mechanical or thermal treatments may result in different borate coordinations and altered network connectivities within the glasses [7,8,26–29]. In the present study, the glass compositions NBS1 and NBS2 are specifically selected to investigate how the mechanical properties are influenced by structural changes, namely the presence of non-bridging oxygen ions, by changes in the boron coordination and also by the network connectivity in terms of homonuclear and heteronuclear bonding.

In order to explain the differences regarding the number of non-bridging oxygen ions, it should be recalled that the addition of network modifier oxides such as sodium oxide to a binary borosilicate glass initially transforms neutral $B\text{O}_3$ units into charged $[B\text{O}_4]^-$ tetrahedra without introducing non-bridging oxygen ions into the network. Due to this transformation more interconnections will be introduced for glass

compositions with up to $R(=Na_2O/B_2O_3) = 0.2$, the boron anomaly line. This also results in a denser structured three-dimensional network compared to vitreous B_2O_3 with its planar $B\text{O}_3$ rings. A further increase in the modifier oxide content, when exceeding the boron anomaly line of $R = 0.2$, leads to the progressive depolymerization of the whole glass network, though non-bridging oxygen ions are only evident in NMR studies for $R > 0.5$ [30,31].

The glass composition of NBS2 lies directly on the line of the boron anomaly $R \sim 0.2$ while NBS1, with the same SiO_2 content, but varied $\text{Na}_2\text{O}:B_2\text{O}_3$ ratio ($R = 1.6$) lies further off in the ternary diagram [7,8, 25–28]. NBS1 is a model for stable borosilicate glasses in which no phase separation occurs, i.e., where no competition is evident in the connectivity between the network cations Si, B_4 , or B_3 (the subscript denotes the boron coordination). NBS2 would show visible phase separation if not for the addition of 1 mol% Al_2O_3 . Previous studies revealed that NBS2 shows preferential bonding in annealed glasses favoring homonuclear $B_3\text{O}-B_3$ and $\text{Si}-\text{O}-\text{Si}$ bonds. Furthermore, the fact, that all modifier oxides in the glass NBS2 are used to transform trigonal $B\text{O}_3$ into $[B\text{O}_4]^-$ tetrahedra, results in a fully polymerized glass with a high viscosity, even at high melting temperatures. The composition of NBS2 places it in the region of metastable immiscibility, which does not occur in the melt, but below the liquidus temperature and the rate of phase separation depends strongly on the cooling rate. Therefore, the combination of high viscosity and the tendency toward preferential bonding leads to a high dependence of the medium range order or connectivity on the cooling rate [26,27]. The two compositions NBS1 and NBS2 are therefore taken as representatives for different structural glass types, i.e., due to different $\text{Na}_2\text{O}:B_2\text{O}_3$ ratios for glasses with and without non-bridging oxygen ions, and the glass NBS2 is selected for its uniform composition which has the capacity to display different connectivities which can be influenced by changes in thermal history alone.

^{11}B -Boron Nuclear Magnetic Resonance (^{11}B NMR) spectroscopy [26] revealed that NBS2 contains $\sim 18\%$ $[B\text{O}_4]^-$ units, whereas the remaining $\sim 82\%$ of borates exist as neutral trigonal planar units inside and outside ring structures, with no evidence for the occurrence of non-bridging oxygen ions. The boron structure of NBS1 glass consists of more than 80% $[B\text{O}_4]^-$ tetrahedra, the remaining 20% borates are found in neutral trigonal borate groups. Thus, non-bridging oxygen ions, which are expected to exist in the NBS1 glass composition, are linked to the silicate groups of the network, forming Q^3 -units (representing SiO_4 tetrahedra with three bridging and one non-bridging oxygen ion), which is in agreement with the Raman spectra [8].

As mentioned above, subtle differences in the glass structure can be achieved by varying the thermal conditions during casting of the NBS2 glass. Similar to melts of crystalline solids, lower coordination numbers are thermodynamically favored at high temperatures [32,33]. Sufficient quenching ideally freezes the lower-coordinated high temperature structure during the transition from liquid to the rigid state, which can lead to a higher proportion of $B\text{O}_2^-$ units in the borate sub-network. However, no significant changes in the boron coordination are observed between the quenched and annealed NBS2 glasses, where the cooling rate dependence is restricted to variations of the connectivity. Combined NMR and vibrational spectroscopic analyses showed that the thermal history especially influences the connectivity between the borate and silicate entities in the NBS2 glass [26,27]. Thus, slowly cooled glasses have more $\text{Si}-\text{O}-\text{Si}$ and $\text{B}-\text{O}-\text{B}$ bonds and only a small portion of mixed $\text{Si}-\text{O}-\text{B}$ bonds. Equilibrium cooling (e.g., furnace cooling) results thus in a higher fraction of more homonuclear bonds; furthermore, $B\text{O}_3$ units in furnace cooled samples are predominantly arranged in boroxol rings, whereas $B\text{O}_3$ entities in quenched NBS2 glass are less often present in ring configurations, but instead more often linked to SiO_4 tetrahedra [26,27]. The B_3/B_4 ratio in NBS2 glasses quenched from a final melting temperature of 1750 °C is only slightly higher than in furnace cooled or quenched NBS2 glasses which were subjected to a final melting temperature of only 1650 °C.

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