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Deformation and cracking behavior of La_2O_3-doped oxide glasses with high Poisson's ratio

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ABSTRACT

Oxide glasses pose high theoretical strength originating from their strong ionocovalent bonding, but they experience amplification of tensile stresses around defects under tensile loading and lack efficient stress dissipation mechanisms. Consequently, glasses exhibit low practical strength and fracture toughness, limiting the scope of their applications. Different strengthening and reinforcement approaches have thus been tested, but relatively little success has been achieved with respect to making the glasses intrinsically more ductile through composition optimization. Following earlier literature reports, a possible route to achieve this would be to prepare glasses with high Poisson's ratio above ~0.32. Yet, no oxide glasses with such high Poisson's ratio have been reported and the mechanical properties of oxide glasses with Poisson's ratio ≥ 0.30 are poorly understood. In this paper, we synthesize 25%La_2O_3–15%Al_2O_3–60%B_2O_3, 25%La_2O_3–15%Al_2O_3–60%SiO_2, and 25% La_2O_3–15%Al_2O_3–60%GeO_2 glasses (fractions in mol%), all exhibiting high Poisson's ratio values (~0.30). We evaluate the mechanical properties, including elastic moduli, Poisson's ratio, hardness, and resistance to indentation cracking of the as-prepared as well as densified glasses. In addition, the indentation deformation mechanism of the glasses along with the accompanying underlying structural changes is investigated. This study therefore presents insight into the composition-property relations of high Poisson's ratio glasses, which may be used in future design of ductile oxide glasses with potential applications in electronic devices, optical fibers, and load-bearing components of buildings or other constructions.

1. Introduction

Overcoming the brittleness of various materials is a recurring challenge in engineering, motivating research into enhancement of ductility and understanding the structural features controlling the deformation and cracking behavior. Such studies are especially important for oxide glass materials, which offer considerable potential for a variety of applications given their transparency, relatively low cost, and high hardness and theoretical strength [1]. However, they are limited by their tendency to brittle fracture [2], which originates from the concentration of stresses around defects such as scratches on the surface [3], and the lack of any efficient shearing mechanism that could dissipate those stresses. Metallic glasses, on the other hand, can in many cases dissipate much more mechanical work compared to oxide glasses through plastic deformations around defects [4], resulting in higher fracture toughness [5]. Two main structural differences between metallic and oxide glasses are (i) higher packing density of the constituent atoms in the former, and (ii) stronger covalent and ionic bonds in the latter [6]. Both packing density and bond directionality influence the deformation behavior of materials. For instance, a densely packed material with non-directional metallic bonding will tend to change its shape when subjected to stress, but resist overall volume change. Conversely, a material with a more open atomic configuration consisting of directional covalent bonds will shrink or expand depending on the direction of the applied stress, but it will attempt to retain its original shape. These deformation modes are conveniently quantified by the Poisson's ratio (ν), which is the ratio between longitudinal and transverse strains of a given material subjected to uniaxial stress.

Poisson's ratio is thus an important material property, which appears to control the ductility of metallic glasses, as shown by Lewandowski et al. [7]. Around $\nu = 0.32$, a dramatic increase in fracture energy with increasing ν is observed for metals, which is referred to

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as the brittle-to-ductile transition. The structural origin of this empirical relation is not yet understood and it has not been experimentally verified in oxide glasses, which feature ionocovalent bonding and typical ν values well below 0.32 (e.g., $\nu = 0.23$ for window glass [8]). However, molecular dynamic simulations indicate that increasing the intrinsic packing density could lead to an enhanced ductility in case of amorphous silica [9], which is also in agreement with the positive correlation between ν and packing density found in various solids [10]. Furthermore, Poisson's ratio also controls the deformation mechanism of glasses, e.g., during sharp contact loading. Low-ν glasses such as amorphous silica densify easily when loaded, since the significant free volume in their networks facilitates compaction [11,12]. On the other hand, high-ν glasses such as bulk metallic glasses usually exhibit efficiently packed networks, which hinders the ability to densify, and forces the material to shear during loading. There is a gradual transition between these two deformation mechanisms with increasing ν, along with an accompanying change in the characteristic cracking pattern observed upon indentation [13]. While most studied oxide glasses exhibit ν values within the range of 0.15 to 0.30, there is limited knowledge on the deformation and cracking behavior around the brittle-to-ductile transition boundary (~0.32).

In this study, we attempt to prepare high-ν oxide glasses in order to investigate whether their deformation and cracking behavior differ from other oxide glasses with lower ν. To do so, we here synthesize three La_2O_3-containing glasses with different network formers and subsequently subject them to high temperature densification (so called hot compression). This is based on literature reports, suggesting that La_2O_3-bearing glasses tend to exhibit high Poisson's ratio values (~0.30) [14–16]. In oxide glasses, La^{3+} ions act as charge-balancing modifier species, similarly to alkali or alkaline earth metal ions, but they form relatively strong bonds with oxygen due to their high field strength (charge-to-size ratio) [17,18]. Moreover, hot compression always leads to an increase in packing density of glasses [19], which in turn scales positively with ν [10]. In order to understand the effect of the network-former on the intrinsic ν value, as well as its susceptibility to change upon compression, we select three different network-formers as the base of the glass network (B_2O_3, SiO_2 and GeO_2 – constituting 60 mol% of the glass network formula in each case), and add fixed amounts of La_2O_3 and Al_2O_3 to each of them (25 and 15 mol%, respectively). Al_2O_3 is included, as it has been found to increase the solubility of La_2O_3 in oxide glasses [20]. This study also provides some insight into the pressure response of complex oxide glasses, which could be important for the development of glasses with tailored properties [21]. As such, we study the composition and pressure dependence of ν, as well as the possible accompanying increase in ductility, by Brillouin spectroscopy and micro-indentation. The morphology of the indentation-induced cracking and deformation mechanisms are further inspected by optical and atomic force microscopy (AFM). Finally, the underlying structural changes occurring due to hot compression and indentation are probed by micro-Raman spectroscopy.

2. Experimental

2.1. Sample preparation

Three glasses containing 25 mol% La_2O_3, 15 mol% Al_2O_3, and 60 mol% B_2O_3, SiO_2 or GeO_2, were synthesized by the traditional melt-quenching technique. Adequate amounts of La_2O_3 (SigmaAldrich, purity > 99.9%), Al_2O_3 (SigmaAldrich, > 99.5%), H_3BO_3 (Honeywell, > 99.5%), SiO_2 (SigmaAldrich, > 99.8%), and GeO_2 (Alfa Aesar, > 99.98%) were first dried and thoroughly mixed. These powder mixtures were then added stepwise to a Pt-Rh crucible and melted in an electric furnace. The melts were homogenized at ~1600 °C for 3 h and quenched by pouring the melt onto a brass plate and pressing with a steel plate. The quenched glasses were transferred to an annealing furnace at their estimated glass transition temperature (T_g), and cooled down to room temperature at a rate of ~5 °C/min. Small specimens of each glass were cut to measure the actual T_g value using differential scanning calorimetry (DSC 449C, Netzsch). T_g was determined as the intercept between the extrapolated isobaric heat capacity of the glass and the tangent to the inflection point of the glass transition peak. The glasses were re-annealed at their measured respective T_g values. We note that the glasses featured minor areas with partial crystallization, which were cut and discarded from further analyses.

Approximately $6 \times 6 \times 2\,mm^3$ specimens were cut from each glass, ground to be co-planar, and polished in water using SiC with grit size up to 4000. For each glass composition, two specimens were subjected to hot compression at 1 and 2 GPa, respectively. These high-pressure treatments were in all cases conducted by heating the glass specimen to their ambient pressure T_g value in an N_2-containing chamber, holding this temperature for 30 min, followed by rapid cooling (~60 °C/min) and decompression at room temperature. Details of the compression chambers are given in Ref. [19]. Density was measured on the annealed and hot compressed samples using Archimedes' principle of buoyancy. The weights of the samples in air and ethanol were recorded ten times.

2.2. Indentation

A Vickers indenter (Duramin 5, Struers) was used to probe the hardness and the resistance to indentation cracking for the as-prepared and hot compressed glasses. The surface of each specimen was re-polished prior to indentation under ambient conditions with relative humidity of 45 ± 5%. Successively increasing loads from 0.245 to 4.91 N were applied, with a hold time of 15 s. Each identical loading cycle was repeated 30 times. Vickers hardness (H_V) was computed from the diagonals of the indent impressions measured using optical microscopy,

$$H_V = \frac{1.8544 \cdot F}{d^2}. \quad (1)$$

where F is the peak load, and d is the average indent diagonal. At each load, the number of cracks emanating from the corners of the indent impressions was counted within ~1 min after unloading. The probability of crack initiation at a given load was then calculated by dividing the total amount of recorded cracks with the maximum number of possible corner cracks (i.e., four per indent). A sigmoidal function was fit to the crack initiation probability vs. load data. Crack resistance (CR) was determined as the load corresponding to 50% crack probability [22].

2.3. Supplementary inspection of indentation imprints

The sub-surface cracking and deformation behavior was further analyzed by considering the cross-sections of Vickers indents. In samples of the as-prepared glasses ($\sim 16 \times 4 \times 0.3\,mm^3$), a line of 15 to 17 indents made at 4 N was created through the middle of each specimen. The distance between each indent center was 300 μm. The glass specimen was then broken into two pieces by bending the specimen with the surface containing indents being on the tensile side. This resulted in two $\sim 8 \times 4 \times 0.3\,mm^3$ specimens. The cross-sections of the indents were then inspected using optical microscopy to investigate the deformation zone and the cracking system beneath the glass surface. Moreover, to inspect the morphology of the sub-surface cracking patterns, five additional indents were made at 4 N in the surfaces of the as-prepared glasses. These glasses were then subjected to polishing with SiC (grit 4000) for ~3 min to remove the outermost surface and images of the remaining indent impressions were recorded using optical microscopy.

Finally, to study the indentation deformation mechanism, ten additional indents were made at 0.25 N in the surfaces of the as-prepared glasses. The relatively low load was chosen to avoid indentation cracking. The indent topography was probed using AFM (Ntegra, NT-MDT), with silicon tip cantilevers (NSG10, NT-MDT) in the semi-