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Indentation deformation mechanism of isostatically compressed mixed alkali aluminosilicate glasses

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ABSTRACT

Oxide glasses can be permanently densified through application of high pressure at room or elevated temperature. Such treatment allows for modification of macroscopic glass properties. However, the structural origins of the pressure-induced property changes are not yet fully understood. In this study, we investigate the ability of a glass network to resist densification under pressure at both ambient and elevated temperatures. We study the detailed deformation mechanisms (densification and shear flow) that occur during indentation of series of as-prepared and isostatically compressed mixed Na/K aluminosilicate glasses, which exhibit a pronounced non-linear scaling in glass properties due to the mixed alkali effect. Following pressure treatment at elevated temperature, an increase in Vickers hardness is observed due to a significant decrease in densification under the indenter. In contrast, the volume of glass developed in the pileup regions due to shear flow is unaffected by the pressure treatment. This change in the relative contributions of these plastic deformation mechanisms can explain the decrease in crack resistance of the glasses induced by the isostatic compression treatment.

1. Introduction

The Achilles heel of oxide glasses is their brittleness, since impact or scratch events can result in the introduction of cracks, which amplify local tensile stresses and can ultimately lead to fracture. To enable new advanced glass applications and fulfill the need for scratch-resistant and mechanically durable glass covers for personal electronic devices, improvements in strength and damage resistance are needed [1–4]. Development of new glass compositions with improved mechanical performance requires a careful balancing of the oxide components, typically involving extensive and time-consuming glass preparation and characterization experiments. Since the macroscopic properties are a direct result of the underlying structure, it is beneficial to improve the understanding of structure–property relations and how these are influenced by changes in chemical composition and post-treatment.

Vickers micro-indentation is a common test to evaluate glasses for personal electronic devices, from which the Vickers hardness (H_V) and crack resistance (CR) can be extracted. In addition to chemical composition, the values of H_V and CR are influenced by various parameters, such as the load applied during indentation [5,6], atmospheric conditions [7–11], processing conditions [12,13], and post-treatment [14]. Various post-treatment methods are currently being applied in the industry to prepare damage resistant glasses with improved values of H_V and/or CR, such as chemical strengthening and thermal tempering. An alternative post-treatment method is the isostatic compression method performed at or around the glass transition temperature (T_g) [15]. Such post-treatment of bulk oxide glasses has been found to increase density, hardness, and elastic moduli permanently, even for applied pressures below 1 GPa [16–18]. Structural studies on isostatically compressed glasses have shed light on major structural changes occurring during densification [19,20], but their relation to changes in macroscopic properties (e.g., hardness) remains poorly understood. Typical pressure-induced structural changes include increasing network-former coordination number and decreasing modifier-oxygen bond distances and inter-tetrahedral bond angles, in addition to modifications of the intermediate range order [19,20].

Recently, we have subjected a series of mixed alkaline earth aluminosilicate glasses to isostatic compression at 1 GPa and T_g in order to gain insight into the mixed modifier effect [15]. The mixed modifier effect concerns the non-additive variations in a wide range of physical properties when one alkali or mixed alkaline earth oxide is substituted for another one at constant total modifier content [21–23]. The effect usually manifests itself as a positive or negative deviation from linearity in transport-dependent properties, such as diffusivity, conductivity,

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viscosity, and hardness [24], but it has also been recorded in static properties such as refractive index and density [23]. In the compressed mixed alkaline earth aluminosilicate glasses, we found that the largest pressure-induced increase of H_V occurs in compositions with approximately equal concentrations of the two modifier oxides [15]. Therefore, it is interesting to investigate the pressure-induced structural changes and deformation mechanism controlling such property changes in mixed modifier oxide glasses.

In addition to being an interesting post-treatment method, high-pressure experiments are also useful for obtaining insights into the indentation deformation mechanism, since high stresses develop in glasses under sharp contact loading. The resistance of a glass to deformation during indentation consists of several contributions: elastic deformation, shear (or plastic) flow, and densification [25–29]. Elastic deformation is a reversible compression that recovers after unloading, shear flow is a volume conservative displacement of matter, and densification is a non-volume conservative irreversible compression that creates a hemispherical area of increased density beneath the imprint [30]. Whereas the elastic response is difficult to measure once the indenter pyramid has been unloaded, the volume contributions associated with the irreversible deformation mechanisms can be quantified by determining the topography of the indent before and after an annealing treatment at $0.9T_g$. This method has been proposed by Yoshida et al. [31] and recently applied in various studies to characterize the indentation deformation mechanism of glasses [30,32–36].

In this work, we investigate the effect of isostatic compression at elevated temperature on the micro-mechanical properties of a series of mixed alkali aluminosilicate glasses and correlate them with the indentation deformation mechanisms (densification vs. shear flow) before and after compression. We study a $Na_2O/K_2O–MgO–Al_2O_3–SiO_2$ glass series with varying Na/K ratio, since it is known to exhibit the mixed alkali effect (MAE) in density and various thermal and mechanical properties [37], enabling the assessment of how the MAE in these properties are affected by the pressure treatment. The contributions of densification and shear flow to indentation are determined using atomic force microscopy (AFM), applying the method developed by Yoshida et al. [31]. The composition and pressure dependences of density, elastic moduli, and overshoot in heat capacity during the glass transition are also determined, which are useful for interpreting the AFM results. Finally, we discuss the effect of compression on the indentation deformation mechanisms in terms of the underlying structural changes and their correlations with the elastic moduli, hardness, and crack resistance.

2. Experimental section

2.1. Sample preparation

The five glasses in the investigated aluminosilicate series ($Na_2O/K_2O–MgO–Al_2O_3–SiO_2$) were prepared by melting the mixed raw materials under continuous stirring for 16 h at 1650 °C in air. The liquids were delivered through a platinum downcomer at a viscosity of approximately 70 Pa s and finally pressed into graphite molds. The procedure is described in more detail elsewhere [37]. The molar concentrations of MgO, Al_2O_3, and SiO_2 were constant and all glasses were peralkaline, i.e., sufficient modifier oxides are available to charge-balance aluminum in four-fold coordination. The total concentration of Na_2O and K_2O was kept constant at ~15 mol% and the $[K_2O]/([K_2O] + [Na_2O])$ ratios of the five glasses are 0.02, 0.20, 0.46, 0.71, and 0.93, respectively. T_g of the glasses, which were determined from viscosity measurements as the 10^{12} Pa s isokom temperature [38,39], are 654, 657, 673, 709, and 782 °C, respectively. The glass samples were cut to dimensions of $25 \times 25 \times 1$ mm^3, annealed at their respective T_g value for 8 h, and finally polished to an optical finish.

Isostatic compression of the samples at elevated temperature was carried out in a nitrogen gas pressure chamber, which contains a multizone cylindrical graphite furnace. Each sample was subjected to an individual treatment at its respective ambient pressure T_g value and an applied pressure of 0.5 or 1.0 GPa. The system was kept at these conditions for 30 min, enabling structural rearrangements of the glass network at the high-pressure/high-temperature environment. Afterwards the samples were first cooled, followed by decompression, at rates of 60 K/min and 30 MPa/min, respectively. The setup used for this pressure treatment has been described in further detail in Ref. [15].

2.2. Characterization

The density values of the glass samples before and after isostatic compression were determined by Archimedes' principle using water as the immersion medium. Each measurement of sample weight was repeated ten times.

The overshoot in the isobaric heat capacity (C_p) of the glasses compressed at 1.0 GPa was determined using a differential scanning calorimeter (DSC 449C, Netzsch). The measurements were conducted using Pt crucibles in a purged argon atmosphere and the C_p curve for each measurement was calculated relative to the C_p curve of a sapphire reference material of comparable mass. Each sample analysis consisted of two up- and down-scans with heating and cooling rates of 10 K/min. The maximum temperature was set to 80 °C above the respective T_g value. Because the glass is heated to $T_g + 80$ °C during the first upscan, the compressed glass has relaxed and recovered its original state before compression with respect to enthalpy [40]. Therefore, the C_p curve of the second upscan reflects that of the glass cooled under standard conditions, i.e., at 10 K/min and atmospheric pressure.

Brillouin light scattering was used to determine the pressure-induced changes in the elastic moduli of samples compressed at 1 GPa. Samples were tested in emulated platelet geometry by placing ~1 mm thick samples with parallel faces on a highly reflective mirror [41,42], which allowed a full determination of elastic constants. A 1-inch achromatic doublet lens (f = 76.2 mm, numerical aperture = 0.15, 90% clear central aperture) was used for laser delivery and for collection of the scattered light. A continuous wave 532 nm green laser was used as the probing light source, delivered with transverse-electric polarization at 200 mW intensity. Brillouin frequency shift was detected by a six-pass high contrast Fabry-Pérot interferometer (JRS Scientific Instruments) by collecting for ~1000 cycles. The elastic moduli of the as-prepared samples were taken from Ref. [37].

Vickers hardness (H_V) and crack resistance (CR) of the glass samples before and after isostatic compression were measured using a Vickers micro-indenter (Duramin 5, Struers A/S). The measurements were performed in air at room temperature. At least 30 indents were performed at each load (0.025, 0.050, 0.100, 0.200, 0.300, 0.500, 1.000, and 2.000 kgf) with a dwell time of 15 s. H_V was calculated from the size of the imprint at each load, whereas CR for each sample was calculated by determining the load leading to formation of an average of two radial cracks from the four corners of the imprint.

To determine the change in indentation deformation mechanism as a result of isostatic compression, the method developed by Yoshida et al. [31] was applied. In this method, it is assumed that no structural (density) relaxation of the glass network occurs upon annealing at $0.9T_g$ for 2 h, but only relaxation of the densified volume due to the indentation. For compressed glasses, this could be problematic, since the pressure-induced bulk densification could partly relax during this annealing, possibly interfering with the relaxation of the indentation densified volume. To the authors' knowledge, this has not yet been investigated and we therefore measured the density relaxation of the compressed samples annealed at $0.9T_g$ for 1, 2, and 3 h.

The volumes of densification (V_d) and shear flow (V_s) were determined for the as-prepared glasses and those isostatically compressed at 1.0 GPa. The indent topographies were imaged using an atomic force microscope (Ntegra, NT-MDT), equipped with silicon tip cantilevers in semicontact mode. The scanning frequency was