



Structure and mechanical properties of compressed sodium aluminosilicate glasses: Role of non-bridging oxygens



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ARTICLE INFO

Article history:

Received 2 February 2016

Received in revised form 15 March 2016

Accepted 16 March 2016

Available online 2 April 2016

Keywords:

Aluminosilicate glass

Structure

Non-bridging oxygen

Pressure

Indentation

ABSTRACT

Clarifying the effect of pressure on the structure of aluminosilicate glasses is important for understanding the densification mechanism of these materials under pressure and the corresponding changes in macroscopic properties. In this study, we examine changes in density, network structure, indentation hardness, and crack resistance of sodium aluminosilicate glasses with varying Al/Si ratio and thus non-bridging oxygen (NBO) content before and after 1 GPa isostatic compression at elevated temperature. With increasing NBO content, the silicate network depolymerizes, resulting in higher atomic packing density, lower hardness, and higher crack resistance. The ability of the glasses to densify under isostatic compression is higher in the high-NBO glasses, and these glasses also exhibit more pronounced pressure-induced changes in mechanical properties. The ²⁷Al NMR data show a surprising presence of five-fold aluminum in the as-made high-NBO glasses, with additional formation upon compression. Our study therefore provides new insights into the complicated relationship between Al coordination and NBO content in aluminosilicate glasses and how it affects their densification behavior.

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1. Introduction

The relationship between structure and properties for sodium aluminosilicate (Na₂O–Al₂O₃–SiO₂) glasses and glass-forming liquids with varying thermodynamic variables (e.g., composition, temperature, and pressure) are important for both industrial and geological processes. These glasses are commercially used for various products, such as flat panel display glass, scratch resistant cover glass, and nuclear waste glass. The three oxides constitute >80% of andesitic and granitic magmatic systems and therefore also have important implications for magma dynamics and properties.

Several structural models have proposed that for Al/Na ratio ≤ 1, i.e., excess Na⁺ ions, all Al³⁺ is found in tetrahedral configuration (Al^{IV}) [1–4]. Addition of Al₂O₃ to an alkali silicate glass ideally leads to the removal of the network-modifying Na⁺ ions from their original role in the network until no more non-bridging oxygen (NBO) atoms remain [5]. For Al/Na ratio ≥ 1, some Al³⁺ ions can no longer be charge balanced in tetrahedral configuration and some excess Al³⁺ is forced into higher coordination number (five-fold Al^V or six-fold Al^{VI}) as a

means of charge-balancing additional Al tetrahedra [6–8]. An alternative hypothesis is that Al^{IV} can be incorporated, even in peraluminous compositions, without the need for a charge-balancing cation through association with a three-coordinated oxygen (oxygen tricluster) [9–11]. In any case, it is well accepted that a range of macroscopic properties (e.g., transport and mechanical) depend on the Al/Na ratio and thus the network connectivity [12–15], i.e., the fraction of NBOs.

Clarifying the effect of pressure on the structure of aluminosilicate glasses is important for understanding the densification mechanism of these materials under pressure and the corresponding changes in macroscopic properties. However, high-pressure experiments are challenging, partly due to the typical small sample volumes [16], prohibiting characterization of post-compression properties. In this work, we investigate sodium aluminosilicate glasses quenched under isostatic pressure from the glass transition temperature in a nitrogen gas pressure chamber. Although this approach is relatively modest in both temperature and pressure (~*T_g* and ≤ 1 GPa), it permits permanent densification of relatively large glass pieces (cm²) that are suitable for characterization of, e.g., mechanical properties [17,18]. This is because permanent densification of glass occurs at significantly lower pressures for compression at elevated temperature compared to that at room temperature [19,20].

Pressure-induced structural changes of aluminosilicates are manifested by changes at both short- and intermediate-range length scales,

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including increase in the local coordination numbers of the network forming Al and Si cations from 4 to 5 and 6, enabling closer packing of the structural units. This coordination number change has been reported to involve conversion of NBO to bridging oxygen (BO) [21–24], but in the absence of NBOs, it can also occur through the formation of oxygen triclusters [25,26]. The densification mechanism of sodium aluminosilicate glasses has also been suggested to include decrease of Na–O bond distances [23,27,28], decrease of inter-tetrahedral bond angles [29,30], decrease of average ring size [31], and increase in distribution of Si–O and Al–O bond lengths [30].

In this work, we study the structure and micromechanical properties of a series of Na₂O–Al₂O₃–SiO₂ glasses before and after isostatic compression at elevated temperature. Specifically we study the influence of NBOs on the changes in structure and properties by varying the Al/Si ratio at constant Na₂O concentration. Our results provide insight into the composition-dependent structural changes that facilitate densification of the aluminosilicate network during compression and the consequence for the micromechanical properties. Improved understanding of the link between structure and mechanical properties is important due to the need for more scratch-resistant and mechanically durable glasses to enable new advanced glass applications.

2. Experimental section

2.1. Sample preparation

We have prepared six glasses in the (75–*x*)SiO₂–*x*Al₂O₃–25Na₂O system with *x* = 0, 5, 10, 15, 20, and 25. In this series, the [Al₂O₃]/[Na₂O] ratio is ≤ 1, and therefore prevailing models of network structure in peralkaline glasses would indicate sufficient charge-compensating Na⁺ ions to keep all Al³⁺ in tetrahedral configuration. High purity powders of SiO₂ (Alfa Aesar; >99.5%), Na₂CO₃ (Sigma Aldrich; >99%), and Al₂O₃ (Sigma Aldrich; ≥99%) were used for glass melting. Homogeneous mixtures of batches (corresponding to ~70 g of oxides), obtained by ball milling, were melted in Pt–Rh crucibles at 1650 °C for 2 h in air. The melts were poured on a metallic table and were initially annealed at 600 °C for 1 h. The chemical compositions of the glasses were determined using flame emission spectroscopy and inductively coupled plasma mass spectroscopy. The results are given in Table 1. To ensure uniform thermal history, the glasses were annealed at their respective glass transition temperature (*T_g*) for ~2 h. *T_g* was determined using differential scanning calorimetry (DSC 449C, Netzsch) at 10 K/min (Table 1). The glasses were cut to dimensions of about 10 × 10 × 8 mm³ and polished to an optical finish.

The six glass compositions were isostatically compressed at 0.5 and 1.0 GPa at their respective ambient pressure *T_g* value (see

Table 1) in a gas pressure reactor with nitrogen as the compression medium. The system was kept at the high-pressure/high-temperature condition for 30 min before cooling to room temperature at 60 K/min, followed by decompression at room temperature at 30 MPa/min. The setup used for this pressure treatment has been described in detail in Ref. [17]. X-ray diffraction analyses showed no evidence of crystallization following the pressure treatment.

2.2. Density

The density values of the as-prepared and compressed glass samples were determined using Archimedes' principle with ethanol as the immersion medium. The weight of each glass sample in both air and ethanol was measured ten times.

2.3. Indentation

Vickers hardness (*H_v*) and crack resistance (CR) of as-prepared and isostatically compressed glasses were measured using a Vickers micro-indenter (Duramin 5, Struers A/S). The measurements were performed in air at room temperature with a dwell time of 15 s. Thirty indentations at each load (0.49, 0.98, 1.96, 2.94, 4.91, 9.81, and 19.6 N) were performed. *H_v* was calculated at 9.81 N from the length of the indentation diagonals. CR was determined as the load leading to an average of two radial/median cracks per indent [35].

2.4. Raman spectroscopy

Raman scattering spectra were measured in backscattering geometry with a Renishaw Invia Raman microscope on freshly polished samples. A diode laser with a wavelength of 532 nm was used as the excitation source. The collected Raman spectra were baseline-corrected using an asymmetric least square algorithm [32]. Afterwards the processed spectra were deconvoluted using Fityk software with Gaussian and Voigt lineshapes.

2.5. ²⁷Al NMR Spectroscopy

²⁷Al magic-angle spinning (MAS) nuclear magnetic resonance (NMR) and triple quantum magic-angle spinning (3QMAS) NMR experiments on both as-prepared and compressed (1.0 GPa) aluminosilicate glasses were conducted at 16.4 T using a commercial spectrometer (VNMRs, Agilent) and a 1.6 mm MAS NMR probe (Agilent) with spinning speeds of 25 kHz. MAS NMR data were acquired using radio frequency pulses of 0.6 μs (equivalent to a π/12 tip angle), relaxation delays of 2 s, and signal averaging of 1000 acquisitions. MAS NMR data were processed using commercial software, without additional apodization and referenced to aqueous aluminum nitrate at 0.0 ppm. A weak background signal from the zirconia MAS rotors was detected by ²⁷Al MAS NMR of an empty rotor and subsequently subtracted from the MAS NMR data of the glass samples. This signal, at approximately 16 ppm, is clearly distinct from the Al peaks in the glasses, but nonetheless has been removed to ensure higher accuracy in the ²⁷Al MAS NMR experiments. Unfortunately, this weak zirconia signal cannot be removed from ²⁷Al 3QMAS NMR data, and appears in some of the spectra as a weak set of contours around 16 ppm in the MAS NMR dimension.

MQMAS NMR spectra were measured using the three pulse, zero quantum filtering method [33]. The hard 3π/2 and π/2 pulse widths were calibrated to 1.8 and 0.7 μs, and the soft reading pulse of the z-filter was optimized to 10 μs. 48 scans were collected for each of 88 *t*₁ points, using a recycle delay of 1 s. Spectra were processed using commercial software (VNMRJ, Agilent) and modest line broadening (100 Hz) was used in processing the ²⁷Al 3QMAS NMR data. For each resonance in the 3QMAS NMR spectra, the centers of gravity in the MAS and isotropic

Table 1

Analyzed chemical compositions (in mol%), calculated number of non-bridging oxygens per tetrahedrally coordinated cation (NBO/T), density (ρ), glass transition temperature (*T_g*), and plastic compressibility (β). Compositions are analyzed using inductively coupled plasma and flame emission spectroscopy, density determined using Archimedes method, *T_g* determined using differential scanning calorimetry at a rate of 10 K/min, and β calculated from the slopes of the linear fits to density vs. pressure for each composition.

Glass ID	Composition (mol%)			NBO/T (–)	ρ (g cm ^{–3})	<i>T_g</i> (°C)	β (GPa ^{–1})
	SiO ₂	Al ₂ O ₃	Na ₂ O				
Al-0	74.7	0.0	25.3	0.677	2.437	470	0.0215
Al-5	70.0	5.1	24.9	0.494	2.456	500	0.0220
Al-10	64.8	10.2	25.0	0.347	2.471	534	0.0221
Al-15	59.6	15.1	25.3	0.227	2.484	595	0.0187
Al-20	54.6	19.7	25.7	0.128	2.494	638	0.0147
Al-25	49.7	25.2	25.1	0.000	2.498	797	0.0157

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