Pressure-driven structural depolymerization of zinc phosphate glass

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ABSTRACT

Understanding pressure-induced structural transformation in glasses is important for designing more damage resistant compositions, since the contact damage that leads to fracture induces high stress levels. However, although phosphorus oxide is an important component in various glasses of industrial interest, knowledge of the structural response of phosphate-based glasses to high pressure remains very limited. In this study, we investigate the influence of hot isostatic compression on the structure, volume densification, and mechanical properties (hardness, crack resistance, and brittleness) of a zinc phosphate glass with O/P ratio = 3.25. Bulk glasses are compressed up to 2 GPa at the glass transition temperature, enabling permanent densification, in turn leading to an increase in hardness and brittleness and decrease in crack resistance. Using Raman and ^{31}P NMR spectroscopy we find that hot compression results in a non-monotonic change in the phosphate network polymerization degree, which is further accompanied by changes in the bond angles and extent of network disorder. We also show that densification during indentation and hot compression is associated with similar structural changes, suggesting that part of the mechanically applied energy during contact damage will be consumed by the pressure-driven structural changes.

1. Introduction

Knowledge of the structure-property transformations of glasses under high pressure is crucial for understanding sharp contact deformation (e.g., indentation), as comparable hydrostatic stresses are reached beneath a sharp indenter during loading. Previous studies have identified important structural and topological rearrangements in oxide glasses either compressed at room temperature or quenched from high pressure, including changes in the next-nearest neighbor (NNN) distributions and ring statistics [1], number of non-bridging oxygen (NBO) [1–3], atomic coordination number of network-former cations [1], and network former- or modifier-oxygen bond distances [2,4]. However, a detailed understanding of the response of inorganic glasses to high pressure is still missing, which limits the possibilities for quantitatively designing more damage resistant glasses [5].

Phosphate-based glasses have received significant attention due to their technological importance attributed to their large thermal expansion coefficients, low optical absorption, and lower glass transition temperatures (T_g) than typical silicate or aluminate glasses [6–8]. Since the pioneering studies by Van Wazer [9], there has been significant progress in the understanding of structure-property relations of phosphate-based glasses using theoretical as well as experimental tools [6,7,10–13]. P_2O_5-containing glasses have found various applications as glass-to-metal seals [14], laser hosts [15], and biomaterials [16], but interestingly P_2O_5 is also included as a component in damage resistant cover glasses in recent patent applications [17–20], although the reasons for this are not well understood in the scientific literature [21–24].

Studies on the influence of high pressure on glass structure and properties date back to the 1950s [25]. Despite the extensive work done in both high pressure glass science and structure-property relations of phosphate glasses [16,26–34], little attention has been devoted to understanding the pressure-induced changes in structure [35–40] and properties of P_2O_5-containing glasses [41,42], as most of the work has focused on silicate, borosilicate, and aluminosilicate glasses with relevance for the geological sciences [1,43]. However, clarifying the pressure-induced structural changes in glass-forming systems with P_2O_5 is crucial for understanding the changes in macroscopic properties and densification mechanisms of multi-component oxide glasses.

In this work, we study a simple binary $60ZnO-40P_2O_5$ glass as zinc

phosphate glasses exhibit relatively good chemical durability [7] and have proved to be suitable probes for understanding structural features of phosphate glasses [44,45]. Moreover, this composition is between the meta- and pyro-phosphate ones, thus having a mixture of structural units with one or two bridging oxygens (BOs), and both types of polyhedra are susceptible for pressure-induced structural changes. As such, the aim of the present study is to shed light on the influence of isostatic compression at elevated temperature on the atomic-scale structure and micro-mechanical properties (hardness H_V, crack resistance CR, and brittleness index c/a) of a model phosphate glass. The structural changes are investigated using micro-Raman and ^{31}P magic angle spinning (MAS) nuclear magnetic resonance (NMR) spectroscopy. We also compare the structural changes during hot compression and indentation.

2. Experimental section

2.1. Sample preparation

To prepare the zinc-rich glass, we first prepared a $50ZnO-50P_2O_5$ glass. ZnO powder was combined with phosphoric acid in a Pt crucible and stirred together. The mix was calcined overnight at 648 K. The crucible was thereafter placed into a furnace at 1373 K for 2 h in air atmosphere. Both bulk glass and roller quenched glass was formed from the melt. Composition of the binary glass was analyzed by inductively coupled plasma optical emission spectroscopy (ICP-OES). The 50–50 binary glass was used as batch material to produce the $60ZnO-40P_2O_5$ glass, by utilizing the analyzed composition and batching the needed amount of ZnO into the crushed glass. This mixture of 50–50 glass and ZnO was melted in a Pt crucible in air for 2 h at 1373 K. The melt was quenched on steel, and the obtained glass upon quenching was transparent and confirmed to be x-ray amorphous. By using ICP-OES, the chemical composition was found to be $60.1ZnO-39.9P_2O_5$. The glass transition temperature (T_g) was determined to be 641 K, using a differential scanning calorimeter (STA 449 F1 Jupiter, Netzsch). The measurement was made under a flow of argon at 40 ml/min. The sample was heated at 10 K/min to 100 K above the T_g in order to relax the sample fully and then cooled at 10 K/min to 313 K. The sample was then subjected to another upscan at 10 K/min. T_g was determined as the inflection point during the second upscan, which reflects the enthalpy response of the sample with a well-defined thermal history (i.e., a known cooling rate). The glass was then annealed for 30 min at T_g to ensure uniform thermal history and glass samples with dimensions of about $10 \times 10 \times 3$ mm^3 were cut and the flats were optically polished. Ethanol was used for the initial stages of grinding and polishing using silicon carbide papers of grit size up to 4000. For final steps of polishing, a lubricant along with diamond suspensions (< 6 μm) was used on a polishing cloth (Struers).

The samples were isostatically compressed at elevated temperature using two nitrogen gas pressure chambers: one vertically positioned with an internal diameter of 6 cm for compression at 1 GPa and one horizontally positioned with an internal diameter of 3 cm for compression at 2 GPa. Multi zone and one zone cylindrical graphite furnaces were used for compression at 1 GPa and 2 GPa, respectively. To monitor the temperature during the experiments, PtRh6%–PtRh30% thermocouples were used. They were arranged in the furnaces and coupled with the input power control electronic systems. In both cases, the pressure was measured by manganin gauges positioned in the low-temperature zone of the reactors. The pressure and temperature were stabilized with an accuracy of 1 MPa and 0.1 K, respectively. Glass samples were placed in an alumina crucible and then heated in the furnaces inside the high-pressure reactors with a constant heating rate of 600 K/h to the desired temperature. The systems were kept at these conditions under high nitrogen pressure (1 and 2 GPa) for 30 min. Afterward, the furnaces were cooled down to room temperature at a constant rate of 60 K/h, while the systems were decompressed with a

rate of 30 MPa/min at room temperature.

2.2. Structural characterization

Raman spectroscopy measurements were conducted at room temperature to obtain structural information at short- and intermediate-range length scales. This was done using a Renishaw in Via micro-Raman spectrometer with 532 nm laser in the range from 200 to 1600 cm^{-1}. The measurements were performed on as-prepared and compressed samples. Furthermore, for the as-prepared glass, the micro-Raman spectrometer was utilized in the mapping mode to acquire spectra at different positions around a Vickers indent produced at 2 kgf. The laser beam was focused on the center of the indent and spectra were collected at interval of 8 μm at 12 different locations away from the center towards the edge and outside of the indent (half-diagonal of the indent was approximately 57 μm). All the recorded spectra were subjected to a baseline correction and area normalization procedure.

Solid state NMR spectra of ^{31}P were obtained using a commercial spectrometer (Agilent DD2) in conjunction with an 11.7 T superconducting magnet (Oxford). All the glass samples were powdered, loaded into 3.2 mm zirconia rotors, and spun with compressed nitrogen at 20 kHz. The resonance frequency of ^{31}P at this magnetic field strength was 202.30 MHz. Spectra were acquired with a 1.2 μs pulse width, corresponding to a $\pi/6$ tip angle, using a delay time of 240 s and as a composite of 60 to 220 free induction decays. Spectra were processed without any additional apodization and referenced to 85% H_3PO_4 in water (0 ppm). Peak fitting was performed using DMFit [46] with Gaussian lineshapes, and consideration of all spinning sidebands was made in determining the Q^n populations.

2.3. Property characterization

Density (ρ) was determined using the Archimedes method by first weighing the sample in air and then weighing it when suspended in ethanol at room temperature. This was repeated a minimum of ten times for each sample. The standard deviation of the reported density values does not exceed $\pm$ 0.002 g cm^{-3}. Molar volume (V_m) was calculated as the ratio between the molar mass of the glass and its density.

A Vickers micro-indenter (Duramin 5, Struers) was used to determine the micro-mechanical properties of samples, i.e., CR, c/a and H_V. The measurements were performed in air at room temperature with relative humidity of 50 $\pm$ 5%. At least 30 indents were performed at each load (0.025, 0.050, 0.10, 0.20, 0.30, 0.50, 1.0, and 2.0 kgf) with a dwell time of 15 s. H_V was calculated from the size of the imprint at each load and measured up to the load resulting in radial/median cracks from all the corners of the indents. CR for each sample was calculated by determining the load leading to formation of an average of two cracks from the four corners of the imprint. The crack-to-indent size ratio (c/a) is measured at a load of 1 kgf, where c is the indentation crack length (distance from indent center to crack tip) and a is the indent's half diagonal.

3. Results and discussion

3.1. Glass structure

Fig. 1a shows ^{31}P MAS NMR spectra of the as-prepared and compressed glasses. Phosphate tetrahedral units are classified using the Q^n terminology, where n represents the number of bridging oxygen per tetrahedron. The NMR spectra of the as-prepared glass is dominated by two isotropic peaks centered around -29 and -12 ppm, with the former peak representing Q^2 tetrahedra (characteristic of metaphosphate chains) and the latter peak representing Q^1 sites that either terminate metaphosphate chains or are found in isolated pyrophosphate dimers [47]. These peak assignments are consistent with those made in