Raman spectroscopy study of pressure-induced structural changes in sodium borate glass

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ABSTRACT

Pressure-induced structural changes in a sodium borate glass have been studied up to ~9 GPa by *in situ* micro-Raman spectroscopy in a diamond anvil cell at ambient temperature. The results show a decrease in the fraction of boroxol rings and an increase in the fraction of non-ring structures with increasing pressure. These findings are compared with Raman spectra of the same glass composition compressed at 1 GPa at its glass transition temperature (406 °C). We show similarities in the medium-range structural changes of the borate glass compressed at high-pressure/low-temperature (9 GPa, 25 °C) and intermediate-pressure/high-temperature (1 GPa, ~400 °C) conditions. The structural changes are elastic during cold compression but inelastic as a result of the hot compression. We discuss this difference in relation to densification and Raman inactive structural changes.

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1. Introduction

An efficient design of new glass materials requires a detailed understanding of their structure-property relations, which remains a key challenge within condensed matter physics. The macroscopic properties of glass depend on the network structure and connectivity, which in turn are a function of chemical composition and state variables such as temperature and pressure. Significant progress has been made in understanding structural variations and structure-property relations across varying compositions and temperatures at ambient pressure, whereas pressure-induced structural changes remain relatively poorly understood [1]. The glass structure can change gradually or abruptly during polyamorphic transition when an isostatic pressure is applied. Moreover, the modification of glass structure and properties depends on the utilized pressure route, *e.g.*, static *vs.* dynamic compression [1] or compression in the rigid *vs.* non-rigid state [2,3].

Densification of glass is often achieved by compression at room temperature (cold compression) in diamond anvil cells (DACs). Combined with *in situ* structural characterization (*e.g.*, vibrational spectroscopy, inelastic X-ray scattering, X-ray and neutron diffraction), this has facilitated the exploration of key structural transformations occurring during densification within a variety of glass systems [4–11]. Using cold compression in DACs, high pressures above 10 GPa can easily be reached, but only small sample specimens can be processed (μm² range). High

pressures can also be reached in multianvil or piston cylinder devices, producing samples typically in the mm² range. This is problematic in relation to analysis of macroscopic properties (*e.g.*, hardness and durability) and for potential industrial applications, where larger sample specimens would typically be required.

Compression of glass at elevated temperature (hot compression) has been found to cause permanent densification at significantly lower pressures than those required in cold compression [12–16], with an accompanying change in the macroscopic properties [17–20]. At room temperature, most pressure-induced structural changes are reversible upon decompression at pressures below 5–10 GPa [1]. Hot compression enables the preparation of bulk sample specimens (cm² range), but while there have been numerous studies of glass structure as a function of pressure at room temperature, there are much fewer examples of the effects of simultaneous pressure and temperature treatment on glass structure [2,13,16,21–22]. The differences and similarities in the structural changes occurring during hot and cold compression are thus not well understood. Improving such understanding could help to clarify the temperature-dependent densification mechanisms of disordered systems and potentially enable predictions of the structural changes occurring during hot compression based on results from cold compression experiments on analogous systems. This could in turn facilitate the development of glasses recovered from hot compression with tailored properties.

The structure of various archetypal glass-forming systems has been studied during cold compression, including vitreous B_2O_3. Borate glasses are interesting model systems for high-pressure studies since

they exhibit significant changes in both short- and intermediate-range order, such as coordination number and fraction of superstructural units (boroxol groups), respectively. For example, compression of vitreous B_2O_3 leads to a breakage of boroxol rings, as supported by molecular dynamics simulations [23,24], Raman spectroscopy [25,26], [11]B 3QMAS (triple quantum magic angle spinning) NMR (nuclear magnetic resonance) spectroscopy [27], ^{11}B NMR spectroscopy [28], and X-ray diffraction results [28]. A polyamorphic phase transition has also been suggested to occur during decompression of vitreous B_2O_3 based on Brillouin scattering data [6,29–31] and molecular dynamics simulations [23].

When adding alkali oxides to B_2O_3 glass, non-monotonic changes in the properties occur since the network-modifying alkali ions can charge-stabilize boron in tetrahedral configuration [32,33]. However, only few high-pressure studies on alkali borate glasses have been conducted [4]. In this work, we investigate the structural changes during cold compression of a sodium borate glass using *in situ* Raman spectroscopy in a DAC. The observed structural modifications are discussed in relation to the changes observed *ex situ* after hot compression of the same glass composition. We emphasize the difference in elastic density increase (*i.e.*, the recoverable deformation) and Raman inactive structural changes as the main difference between hot and cold compressed samples.

2. Experimental procedure

The nominal sample composition used for both cold and hot compression studies was $15Na_2O$-$85B_2O_3$ (mol%). The glass was produced from analytical grade H_3BO_3 and Na_2CO_3 powders, mixed according to the nominal composition and added stepwise to a $Pt_{90}Rh_{10}$ crucible at 1073 K for degassing. The mixture was then heated to 1273 K and kept for 1 h. Afterwards it was heated to 1323 K and kept at this temperature for 15 min to ensure bubble removal before it was finally quenched to room temperature. The glass was annealed at its glass transition temperature ($T_g = 679$ K) for 2 h to remove internal stress and then left overnight at 523 K. To avoid hydration, which is a common problem for borate glasses [34], the glass was kept dry in desiccators with silica gel. The chemical composition was analyzed using wet chemistry method and found to be $15.4Na_2O$-$84.6B_2O_3$ (mol%).

Raman spectroscopic measurements were performed on a Horiba LabRAM HR800 spectrometer with an Olympus SLMPlan 50× objective lens with numerical aperture (NA) = 0.45. A continuous wave 532 nm green laser was used as the probing light source. A membrane-driven DAC with diamond anvil culet size of 400 μm was used for the cold compression experiment, with cryogenically loaded argon used as the pressure transmitting medium. The pressure inside the DAC was monitored from the fluorescent shift of ruby balls placed inside the sample chamber [35]. Following each step of pressure change in the DAC, an equilibration time of minimum 20 min was allowed before the Raman spectrum was collected. Several hours of equilibration time has previously been found to be required to achieve pressure equilibration in B_2O_3 glass [7], whereas this was not needed in the case of lithium borate glasses [36]. A general increase in background intensity was observed in the Raman spectra with increasing pressure inside the DAC. The Raman spectra were first processed by applying a background subtraction, using an asymmetric least squares baseline correction, followed by an area normalization procedure, where total area was transformed into constant area for all spectra [37]. All of the processed spectra were subsequently deconvoluted using Fityk software with Gaussian and Voigt lineshapes. Three separate deconvolutions were performed for each Raman spectrum. The deconvolution parameters presented in Figs. 3 to 5 represent average values from the three deconvolutions, with the error bars representing the standard deviations. An example of a deconvoluted Raman spectra is shown in Fig. 1. Due to fluorescence from the diamonds in the DAC, only the middle frequency region of the Raman spectra was analyzed (350 to 1000 cm^{-1}).
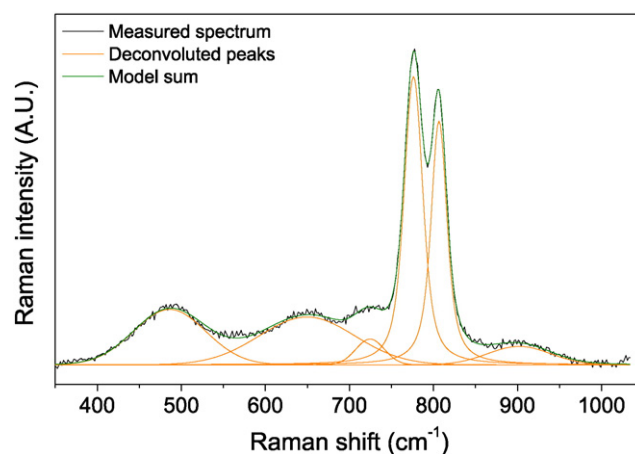

Fig. 1. Example of deconvoluted Raman spectrum of the sodium borate glass measured *in situ* at 1.4 GPa. Voigt lineshapes are used to fit the two main bands (770 and 805 cm^{-1}), whereas Gaussian lineshapes are used for the remaining bands.

Hot compression was performed by isostatically compressing a sample at 1 GPa at its ambient pressure T_g value in a vertically positioned gas pressure chamber, as described in detail elsewhere [17]. The general setup consists of a multizone cylindrical furnace, which is placed inside a gas pressure reactor with nitrogen as the compression medium. The samples were heated at a constant rate of 600 K/h to T_g and the pressure was increased to 1 GPa. The samples were kept under these conditions for 30 min before the temperature was decreased to room temperature at a rate of 60 K/min, followed by decompression at a rate of 30 MPa/min. X-ray diffraction analysis showed no sign of crystallization. The glass transition temperature is a function of pressure [38], but the change is expected to be small within this pressure regime [39]. The Raman spectrum of the hot compressed sample was then collected *ex situ* as described above.

3. Results and discussion

3.1. Structural changes during compression in DAC

In situ Raman spectra of the sodium borate glass during cold compression are shown in Fig. 2a. The most prominent features are the two sharp peaks around 800 cm^{-1}, which are characteristic of alkali borate glasses with less than 20 mol% alkali oxide [40–42]. The peaks in the spectra can be deconvoluted and assigned to the following structural units: 450 cm^{-1} (loose BO_4 [43]), 650 cm^{-1} (loose BO_3 [44]), 770 cm^{-1} (symmetric breathing vibration of triborate and/or tetraborate rings [45–48]), 805 cm^{-1} (symmetric breathing vibration of boroxol ring [49–53]), and 910 cm^{-1} (triborate and/or tetraborate [45,46]).

During compression, all Raman peaks decrease in intensity, except for the peak near 650 cm^{-1}, which increases in intensity. Peak positions of the two sharp peaks at 770 and 805 cm^{-1} increase (Fig. 3), and the intensities decrease, approximately linearly with the applied pressure (Fig. 4). Complete suppression of the 805 cm^{-1} peak has previously been found to occur during cold compression of vitreous B_2O_3 at 11 GPa, in which case the peak position and intensity were also found to vary linearly with pressure [25]. The intensity of the 650 cm^{-1} peak increases approximately linearly with pressure (Fig. 5), whereas the position shifts towards lower frequencies (Fig. 2). This is surprising, since a shift towards higher frequencies is typically seen for Raman peaks during compression across a wide range of vibrational modes and compositions, including silicates [54–56], germanates [57,58], solid argon [59,60], and carbon based solids [61,62]. We should note that the intensity of the 650 cm^{-1} Raman peak is relatively small compared to the background level, *i.e.*, any subtle changes in background can cause