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.

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 (μm^2 range). High pressures can also be reached in multianvil or piston cylinder devices, producing samples typically in the mm^2 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 compression, most structural changes are reversible upon decompression at pressures below 5-10 GPa [1]. Hot compression enables the preparation of bulk sample specimens (cm^2 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 would provide information on 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 archetypical glass-forming systems has been studied during cold compression, including vitreous B_2O_3 . Borate glasses are interesting 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 occurring *ex situ* upon 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 $15\text{Na}_2\text{O}-85\text{B}_2\text{O}_3$ (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 Pt₉₀Rh₁₀ 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 15.4Na₂O-84.6B₂O₃ (mol%).

Raman spectroscopic measurements were performed on a Horiba LabRAM HR800 spectrometer with an Olympus SLMPlan 50x 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 μ m 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 B₂O₃ 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).

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], germinates [57,58], solid argon [59,60], and carbon based solids [61,62]. We should note that the intensities of the Raman peaks are relatively small compared to the background level, i.e., any subtle changes in background can cause changes in peak intensities. However, the background remains flat and uniform throughout the experiment with increasing pressure inside the DAC.

3.2 Structural changes during decompression in DAC

In situ Raman spectra of the sodium borate glass during decompression are shown in Fig. 2b. During decompression from ~9 GPa, the peak positions follow the reverse route as during compression. To illustrate this, the deconvoluted positions of the two main peaks (around 770 and 805 cm^{-1}) are shown in Fig. 3 as a function of pressure. A discontinuity in the Raman and Brillouin peak positions has previously been observed during decompression of vitreous B_2O_3 in the low pressure range [6,25,29-31], but no discontinuity is found for the present sodium borate glass.

During decompression, the intensities and widths of the Raman peaks are reversible (i.e., elastic deformation), except for the peaks at 650 (loose BO_3), 770 (triborate and/or tetraborate rings), and 805 cm^{-1} (boroxol rings). To illustrate this, the peak intensities of the 770 cm^{-1} and 805 cm^{-1} Raman peaks are shown as a function of pressure in Fig. 4, whereas the pressure dependence of the peak intensity of the 650 cm^{-1} peak is shown in Fig. 5. These peaks have been suggested to represent structural features involved in the network densification [26,27,28,63], indicating that permanent densification occurs following cold compression of the sodium borate glass at ~9 GPa. However, the pressure-induced density increase of cold compressed B_2O_3 glass (up to 9 GPa) has been found to relax over the course of days [64], i.e., the absent relaxation of the Raman peak intensities for the present sodium borate glass could be a result of slow structural recovery rather than a result of permanent densification.

3.3 Densification mechanism during cold compression

The pressure-induced decrease in the intensities of the Raman peaks representing ring structures (770 cm^{-1} and 805 cm^{-1}) and the accompanying increase in the intensity of the Raman peak representing loose BO_3 (650 cm^{-1}) indicates a conversion of ring BO_3 into non-ring BO_3 during cold compression. The sodium borate

glass is structurally analogous to $v\text{-B}_2\text{O}_3$ and is therefore expected to behave similarly under pressure and a breakage of boroxol rings has indeed been observed during cold compression of $v\text{-B}_2\text{O}_3$ by molecular dynamics simulations [23,24], neutron diffraction [64], and Raman spectroscopy [25] data. Furthermore, breakage of boroxol rings has also been found following hot compression of $v\text{-B}_2\text{O}_3$ based on Raman spectroscopy [26], ^{11}B 3QMAS NMR spectroscopy [27], ^{11}B NMR spectroscopy [28], and x-ray diffraction [28] data. However, recently a reaction scheme involving the stacking of boroxol rings, rather than dissolution of the rings, has been suggested based on oxygen K-edge spectra of cold compressed $v\text{-B}_2\text{O}_3$ [7]. The reconfiguration of ring structures within the borate network under pressure is an ongoing research topic.

Compared to $v\text{-B}_2\text{O}_3$, less structural data are available for compression of alkali borate glasses. Based on the Raman spectra presented in this study, a conversion of rings into non-rings is considered to be the most likely scenario for the sodium borate glass. The conversion of rings into non-rings has been suggested as the main densification mechanism of $v\text{-B}_2\text{O}_3$ [26-28,64], but we have recently found that even though this structural conversion is observed following hot compression of the sodium borate glass, it could not account for the density changes during subsequent ambient pressure annealing [65]. The major difference between the structural changes observed for B_2O_3 glass and those observed in the present $15.4\text{Na}_2\text{O}-84.6\text{B}_2\text{O}_3$ glass is that in the B_2O_3 glass, only boroxol rings are converted into loose BO_3 groups, whereas in the present sodium borate glass, triborate and/or tetraborate groups are also converted into loose BO_3 groups. Changes in boron coordination are also expected at elevated pressure [36], but these have been found to be fully reversible during decompression [63], even if permanent densification is achieved [7].

3.4 Comparison of cold and hot compression

The conversion between ring and non-ring units discussed above is observed *in situ* during cold compression of the sodium borate glass and also following hot compression of the same glass composition at 1 GPa at its glass transition temperature. Fig. 6 shows a comparison of the Raman spectra of the cold compressed (*in situ*) and hot compressed (*ex situ*) sodium borate glass. Here it can be seen that hot and cold compression causes the same qualitative changes in the Raman spectra. For example, an increase in the 650 cm^{-1} peak upon compaction of the glass. The spectrum shown for cold compression is taken at 1.4 GPa, i.e., within the

elastic regime of densification. However, the pressure-induced structural changes are more pronounced than those found in the permanently densified hot compressed glass. This shows that the structural changes monitored by Raman spectroscopy can occur elastically during cold compression and in-elastically during hot compression.

In a recent study, we found that density changes in the sodium borate glass after hot compression and during subsequent ambient pressure annealing (volume relaxation) were not governed by structural changes detectable by Raman spectroscopy [65]. This indicates that the densification mechanism is Raman inactive. Other structural probes may, however, be capable of monitoring Raman inactive structural changes, displaying the differences in structural changes occurring following hot compression (permanent densification) and during cold compression (elastic densification). For example, a recent study on a boroaluminosilicate glass has showed a decrease in the ^{11}B MAS shift after hot compression, whereas an increase in the ^{11}B NMR shift has been observed *in situ* upon cold compression [63]. The decrease of the ^{11}B NMR shift upon hot compression and increase upon cold compression in the boroaluminosilicate glass indicates that fundamentally different structural changes occur during hot and cold compression. Differences in the structural changes during hot and cold compression have also recently been found for vitreous SiO_2 , i.e., hot and cold compressed SiO_2 glasses with similar densities have different network structures [66]. Moreover, cold compression has been found to result in a more heterogeneous glass structure than hot compression [16].

A conversion of rings into non-rings is evident from the Raman spectra during both hot and cold compression of the sodium borate glass (Fig. 6). That is, the Raman peaks found to exhibit intensity increase (decrease) following hot compression also exhibit intensity increase (decrease) during cold compression. However, Raman inactive structural changes may behave differently during hot and cold compression, as recently found for a boroaluminosilicate glass [63]. The conversion between ring and non-ring BO_3 is expected to require the breakage of chemical bonds, but occurs elastically during cold compression and inelastically during hot compression. This behavior could be explained if the conversion between ring and non-ring BO_3 is a byproduct of increased density, whether transient or permanent. However, density increase is governed by Raman inactive structural changes. That is, if the Raman inactive structural changes behave

elastically during cold compression, the density would recover and consequently also the related Raman active structural changes. On the other hand, if the Raman inactive structural changes are permanent following hot compression, densification and Raman active structural changes would also both be permanent.

4. Conclusion

We have performed *in situ* Raman spectroscopy measurements on a sodium borate glass at pressures up to ~9 GPa at room temperature. With increasing pressure, a decrease in the fractions of six membered triborate, tetraborate, and boroxol rings has been found to occur concurrent with an increase in the fraction of non-ring BO_3 groups. These pressure-induced structural changes have been compared with those from *ex situ* Raman spectroscopy measurements on the same sodium borate glass, which has been subjected to compression at 1 GPa at its glass transition temperature. Qualitatively the same changes are identified in the Raman spectra as a result of both cold and hot compression and our results imply that Raman inactive structural changes govern pressure-induced densification. This may explain how the same changes in the Raman spectra can occur elastically during cold compression and inelastically during hot compression, since these structural changes may be governed by density, which in turn is governed by Raman inactive structural changes.

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FIGURES

Figure 1. Example of deconvoluted Raman spectrum sodium borate glass *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.

Figure 2. *In situ* micro-Raman spectra of sodium borate glass during (a) cold compression up to ~9 GPa and (b) subsequent decompression. Spectra are shifted vertically for clarity. Major changes in peak intensities and positions are seen for the two main peaks (around 770 and 805 cm⁻¹) as well as for the 650 cm⁻¹ peak. Peaks gradually recover during decompression. A mild smoothing algorithm has been applied to the spectra of the as-prepared sample and those acquired during decompression due to their relatively high noise-to-signal ratio.

Figure 3. Positions of the two main Raman peaks (around 770 and 805 cm^{-1}) during *in situ* cold compression and *ex situ* after hot compression at 1 GPa. Positions of Raman peaks in the as-prepared glass is included for comparison. A monotonic increase in the peak positions with pressure is found for both peaks during cold compression, with an elastic recovery during decompression. The lines are guides for the eye. Error bars are smaller than the size of the symbols.

Figure 4. Intensities of the two main Raman peaks near 770 and 805 cm^{-1} during *in situ* cold compression and *ex situ* after hot compression at 1 GPa. The results of the as-prepared glass are included for comparison. Error bars represent standard deviations for three individual deconvolutions of the Raman spectra.

Figure 5. Intensity of the 650 cm^{-1} Raman peak during *in situ* cold compression and *ex situ* after hot compression at 1 GPa. The result of the as-prepared glass is included for comparison. Error bars represent standard deviations for three individual deconvolutions of the Raman spectra.

Figure 6. Comparison of Raman spectrum of the as-prepared sodium borate glass with that of the same glass subjected to hot compression and an *in situ* spectrum collected during cold compression at a pressure similar to that of the hot compressed sample (1.0 and 1.4 GPa, respectively). All of the peaks exhibit changes in intensities upon compression (except the 450 cm⁻¹ peak), including shifts in the peak positions.