# Spectroscopic Evidence of Polymorphism in Vitreous $B_2O_3$

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Brillouin and Raman spectroscopy were performed on $B_2O_3$ glass compressed to 57 GPa at 273 K. Upon compression the sound velocities increase smoothly and the boroxol ring Raman mode vanishes by 11 GPa. Upon decompression the sound velocities follow a different path and at 3 GPa a discontinuity of 3 km/s in $V_p$ and 2 km/s in $V_s$ returns the velocities to the values seen on compression. After the transition, the boroxol ring Raman mode reappears. A second pressure cycle produces the same behavior, suggesting the 3 GPa transition occurs between vitreous polymorphs with different boron coordination.

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According to the traditional perception of the amorphous state of matter, local structural environments vary within a glass. Any changes in the structure should therefore take place in a spatially uncorrelated fashion and from a macroscopic perspective appear to occur gradually. However, for a number of glass-forming systems, such as amorphous ice [1], silica [2,3], germania [4], and yttria metaphosphate [5], abrupt transformations from one structure to another have been observed under the influence of pressure. These abrupt transformations, which are reminiscent of the behavior of crystalline materials, have prompted the notion that there may be "vitreous polymorphs."

The literature suggests that among inorganic materials such polyamorphic transitions are prevalent in tetrahedrally coordinated network glasses, while three-coordinated ones act quite differently under pressure. For the latter type of glasses Grimsditch *et al.* [4] showed that $As_2S_3$ follows the same sound velocity-pressure path upon compression and decompression (up to 4 GPa), while $B_2O_3$ exhibits a closed, gradual hysteresis (upon maximum compression to 15 GPa). These smooth, continuous changes are more indicative of gradual rearrangements in a random network than of a sharp transition between structurally distinct polymorphs. In contrast, the experimental results presented in this Letter suggest that vitreous polymorphs do exist in vitreous $B_2O_3$ and that the transitions between vitreous polymorphs can be abrupt.

The $B_2O_3$ sample for our experiment was prepared by heating reagent grade $B_2O_3$ at 1000 °C overnight in air. To shape the glass into pieces convenient for incorporation into a diamond anvil cell (DAC), two polished Pt plates spaced 30 $\mu$m apart were dipped into the $B_2O_3$ melt, and after allowing 5–10 min for capillary forces to draw the $B_2O_3$ between the platinum plates, the plates were quickly removed from the furnace, placed in a vacuum dessicator, and moved into a nitrogen-purged glove box. After extraction from between the parallel Pt plates, the $B_2O_3$ sample was loaded into a piston cylinder DAC, along with several ruby chips that acted as pressure sensors. Pressure was applied to seal the sample chamber before the diamond cell was removed from the glove box. No pressure medium was employed. Using this procedure, contamination of $B_2O_3$ with water during handling at room temperature was avoided.

Brillouin and Raman spectroscopy were performed using the 514.5 nm line of an Ar-ion laser. The experimental setup is described by Sinogeikin *et al.* [6]. Brillouin spectra were collected for both platelet forward scattering ($\theta = 50°$) and backscattering ($\theta = 180°$) geometries. The scattering geometry was calibrated using an MgO standard and found to be within 0.1°. In platelet geometry the sound velocity $v$ is related to the Brillouin frequency shift $\Delta\omega_P$ according to $v = \lambda_{\text{laser}}\Delta\omega_P/(2\sin 25°)$. While this is sufficient to determine the sound velocity, a second measurement in the backscattering mode, where $v = \lambda_{\text{laser}}\Delta\omega_P/(2n)$, allows one to also determine the refractive index $n$. When the longitudinal sound velocity of $B_2O_3$ exceeds 11.5 km/s (i.e., above 23 GPa on compression and 11 GPa on decompression) the corresponding peak in the forward-scattered Brillouin spectrum becomes obscured by the diamond anvil shear peak. In this regime, however, the refractive index was found to level at a constant value of 1.76 [7]. At high pressures, the longitudinal sound velocity was therefore determined from backscattering spectra using $n = 1.76$.

In the course of the experiment, Brillouin and Raman data were first taken on compression from 6.9 to 52.7 GPa and on decompression from 52.7 to 1.8 GPa. To determine if the observed behavior could be reproduced, the cell was again compressed from 1.8 to 56.8 GPa and decompressed from 56.8 to 0.8 GPa. During the first pressure cycle, the sample was equilibrated at each pressure for at least 12 h and during the second pressure cycle for at least 4 h before being analyzed. Once equilibrated, the pressure on the sample was measured using the ruby fluorescence method [8]. The pressure was measured before and after collecting Raman and Brillouin spectra, and within experimental accuracy, the same pressure was recorded.

The results of the Brillouin and Raman measurements are shown in Figs. 1 and 2, respectively. Upon compression the sound velocities smoothly increase and the 808 $cm^{-1}$ mode, which has been attributed to the symmetric breathing of boroxol rings [9], decreases in intensity until it disappears near 11 GPa. No Raman modes were seen above 11 GPa. (Grimsditch *et al.* [10] saw boroxol rings as high as 14 GPa, both upon compression and decompression. However, the intensity of the 808 $cm^{-1}$ mode in their experiments dropped suddenly near 11 GPa upon compression. We believe that the persistence of the 808 $cm^{-1}$ in Grimsditch's experiment can be attributed to equilibration times of only tens of minutes at each pressure, leaving insufficient time for the glass to transform to a higher-pressure state. Indeed, recent work [11] has suggested that it takes at least several hours for $B_2O_3$ to equilibrate at each pressure.)

Upon decompression the sound velocities follow a different path, remaining higher and exhibiting smaller pressure dependence. The sound velocities decrease smoothly until a sharp transition occurs between 3 and 2 GPa, upon which the sound velocities return to the path followed during compression. At the completion of the transition near 2 GPa, the 808 $cm^{-1}$ boroxol ring mode suddenly reappears along with a Raman mode at 881 $cm^{-1}$. Both modes persist to lower pressure. The 881 $cm^{-1}$ Raman mode has previously not been observed in pure $B_2O_3$. This mode could possibly be attributed to a B-OH stretching, because its frequency matches that of the breathing mode of trigonal B-$(OH)_3$ units in crystalline boric acid ($H_3BO_3$) [12]. The estimated amount of water that dissolves in $B_2O_3$ upon equilibration in air at 1000 °C is sufficient to modify 0.08% of the network bonds [13], which is unlikely to affect the structural integrity significantly. If indeed B-OH units produce this Raman signal, they must be dissolved in the glass because additional Brillouin lines that would indicate the presence of a second phase were never observed. (Raman and Brillouin spectra were collected from the exact same sample volume.)

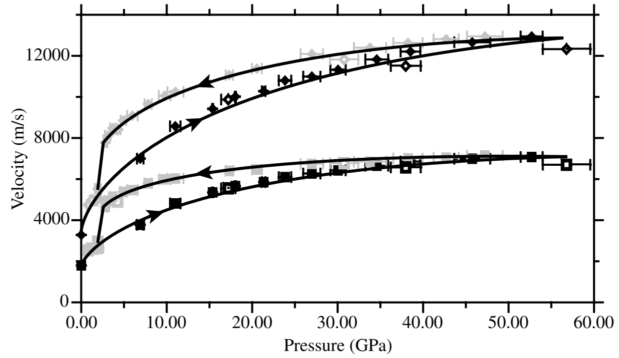

FIG. 1. Compressional and shear sound velocities of boron oxide with pressure. Squares are shear velocities and diamonds are compressional velocities. Solid and open symbols indicate data taken during the first and the second cycle, respectively. Black symbols were taken on pressure increase, gray symbols on pressure decrease. Arrows indicate the direction in which the measurements were taken. Room pressure data were obtained outside the DAC from a different $B_2O_3$ sample.

Further, the mechanical and structural response of $B_2O_3$ glass to pressure is entirely reproducible. During a second compression-decompression cycle the sound velocity data follow that of the first cycle, as shown in Fig. 1. On compression, both Raman modes disappear below 17 GPa and on decompression they reappear after the

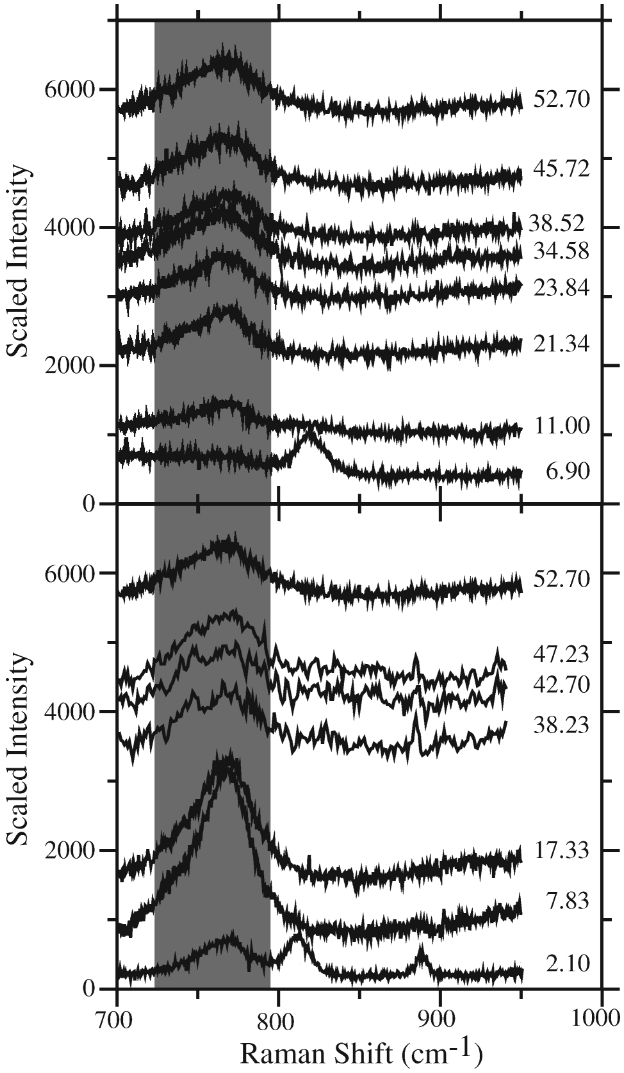

FIG. 2. Stacked $B_2O_3$ Raman spectra for the first pressure cycle. The top panel shows Raman spectra during compression, and the bottom panel during decompression. The peak at 760 $cm^{-1}$ is fluorescence from the diamond anvils, the peak at 812 $cm^{-1}$ is the boroxol ring mode, and the peak at 881 $cm^{-1}$ is a previously unidentified Raman peak. The baseline of each spectrum has been shifted by an amount equal to 100 times the pressure at which the spectrum was collected. The number to the right of each spectrum is the pressure at which it was collected.

abrupt drop in sound velocity, which occurs again just below 3 GPa.

The monotonous changes in the sound velocity as well as the gradual decrease in the intensity of the 808 $\mathrm{cm}^{-1}$ Raman mode during compression suggest a continuous rearrangement of the structure with pressure. In contrast, during decompression the glass exhibits a large discontinuity in properties at about 3 GPa. The fact that this behavior is reproducible suggests that $B_2O_3$ is undergoing a reversible transition between well-defined structural states. What is remarkable, though, is that the transition from low- to high-density amorphous $B_2O_3$ is gradual while the reverse transition is abrupt, bearing the signature of a first-order transformation. Specific trends revealed by our measurements, analyzed in the context of existing knowledge about $B_2O_3$, allow us to further clarify the nature of this transition.

In crystalline form, boron oxide can exist as low-density $\alpha$-$B_2O_3$ (space group $P3_1$) or as high-density $\beta$-$B_2O_3$ ($Ccm_2$). A principal difference between these two structures is the coordination of boron by oxygen, which is trigonal in $\alpha$-$B_2O_3$ and tetrahedral in $\beta$-$B_2O_3$. Interestingly, the transformation between $\alpha$- and $\beta$-$B_2O_3$ at room temperature occurs at about 2 GPa [14], which is close to the pressure at which we observe the sudden drop in the sound velocities. However, we rule out that our sample actually crystallized during decompression, on the grounds that (i) the sound velocities returned to those exhibited by the glass conpression, (ii) during a second pressure cycle the sound velocities and the 808 $\mathrm{cm}^{-1}$ Raman mode behaved just as they did during the first pressure cycle, and (iii) the dramatic increase in scattering intensity typically associated with the formation of grain boundaries during crystallization was not observed.

Instead, we submit, as have previous authors [10], that while in amorphous $B_2O_3$ at ambient pressure boron is entirely three coordinated, an increasing number of boron atoms are converted to tetragonal coordination upon densification. Furthermore, the step change in sound velocities at 3 GPa upon decompression is the result of the abrupt reversal of this coordination change. The apparent differences in the mechanisms invoked upon compression and decompression can be explained as follows.

Given the structural disorder in amorphous materials, the applied stress during compression is transmitted non-uniformly across the structure; i.e., the local strain as reflected by the changes in bond lengths and bond angles varies considerably from one building block to another. Transitions from three- to four-coordinated boron therefore occur first at locations of highest stress intensity. Such a conversion to a more compact structural building block relieves stress in the immediate surroundings, and subsequent transitions require futher pressure buildup. This explains why the changes in glass properties occur gradually over a wide pressure range during densification. Moreover, the changeover from three- to four-coordinated boron, a process that is characterized by a relatively low activation barrier of 36.5 kJ/mol, has been suggested as the mechanism for dissolution of boroxol rings [15] and is therefore also consistent with the disappearance of the mode at 808 $\mathrm{cm}^{-1}$ from the Raman spectra.

Another interesting feature concerning the densification behavior of $B_2O_3$ glass is revealed by comparing the reverse process for different compression maxima. Sound velocity data for compression-decompression cycles up to 13.5, 18.8, and 52.7 GPa, respectively, are shown in Fig. 3. In all cases, the sudden drop in sound velocities associated with the delayed reverse transition takes place at the same pressure and involves the same beginning and ending sound velocity magnitudes, independent of the maximum pressure to which the sample had been compressed (at least for samples compressed to above 13.5 GPa). This indicates that all the structural transitions that are being reverted upon the sudden drop in sound velocities had been the first ones to be invoked upon compression and that these transitions reach completion at relatively low pressure. Moreover, at the top of the reverse transition, i.e., at the lowest pressure to which the four-coordinated structure persists, the sound velocity is approximately the same as that observed upon compression at ~11 GPa, where the characteristic boroxol ring peak disappears from the Raman spectra. This supports the notion that a similar structural state, characterized by the same sound velocities of 8.0 and 4.7 km/s for longitudinal and shear waves, respectively, is achieved at about 11 GPa upon compression and 3 GPa upon decompression, and that

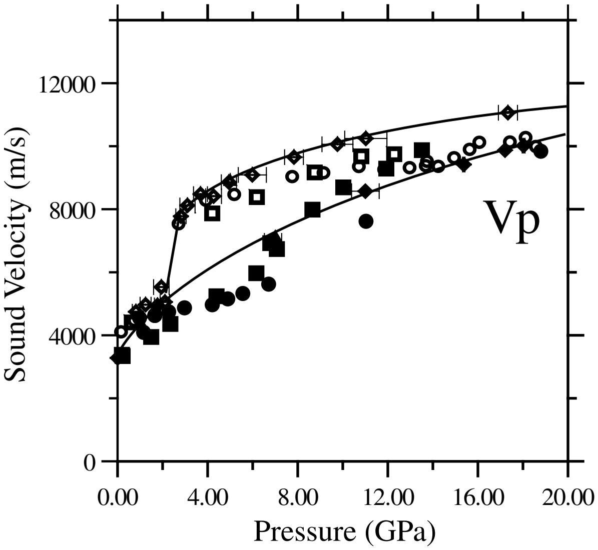

FIG. 3. The longitudinal sound velocity behavior for several $B_2O_3$ runs. Solid and open symbols represent data taken on compression and decompression, respectively. Diamonds and dark lines represent data from the first pressure cycle of the current study, for which the maximum pressure was 52.7 GPa. Squares and circles are from Nicholas *et al.* and represent data taken to a maximum pressure of 13.5 and 18.8 GPa, respectively [16].

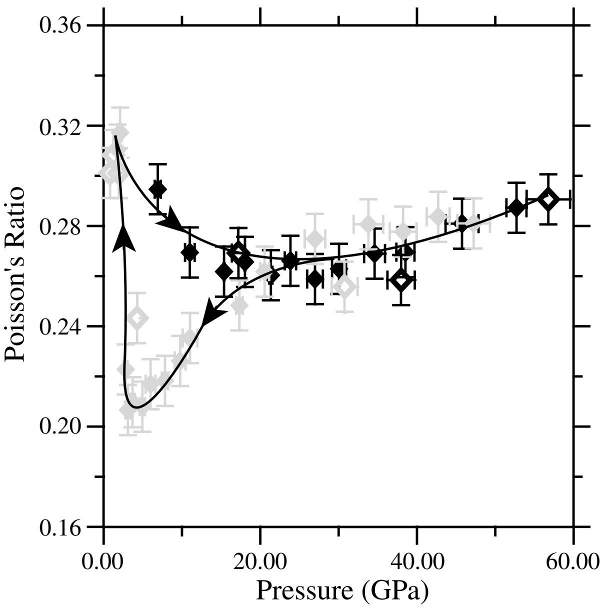

FIG. 4. The Poisson ratio of boron oxide with pressure. Black and gray symbols represent data taken on compression and decompression, respectively. Solid symbols were taken during the first compression cycle and open symbols during the second compression cycle. The Poisson ratio ($\sigma$) was calculated from the sound velocities according to $\sigma = [v_P^3 - 2v_S^2]/[2(v_P^2 - v_S^2)]$.

this state corresponds to the lowest-density structure of a primarily four-coordinated high-density vitreous polymorph of $B_2O_3$.

Note that upon further compression beyond 11 GPa, additional structural relaxation takes place. The fact that, in terms of sound velocities, the decompression paths deviate from the compression paths, and that they all differ from one another if the specimen is compressed to different maximum pressures, establishes that these high-pressure structural changes involve more than just elastic deformations. On the other hand, the Poisson ratios on compression and decompression coincide above 20 GPa, as can be seen in Fig. 4. This suggests that the degree of connectivity within the glassy network is not affected by density changes at these elevated pressures.

Below 20 GPa, however, the Poisson ratio on decompression rapidly drops below that on compression. In this regime, the elastic response perpendicular to the direction of the applied stress is much less than parallel to it. Decoupling between elongation and cross contraction leads to the creation of free volume between structural units. This reveals that upon decompression, a significant activation volume is required to facilitate the reverse transition from four- to three-coordinated boron. During the preceding compaction most of the free volume in the glass had been eliminated, resulting in dense packing of $BO_4$ units. This and the steric constraints associated with tetrahedrally bonded structural units reduce atomic mobility dramatically, resulting in a delayed reverse transformation. When releasing the pressure, free volume develops uniformly across the expanding structure; since compaction was nonelastic, a mere restitution of void space at the original locations is unlikely. Once the necessary activation volume is achieved, the overdue transformation from four- to three-coordinated boron occurs percipitously, affecting all units simultaneously.

In summary, we have shown evidence that vitreous polymorphs exist for boron oxide, an inherently trigonally coordinated network former, and that the transition between these polymorphs is gradual in one direction but abrupt in the reverse direction. In the case of $B_2O_3$ it seems that the basis for polyamorphism is a change in cation coordination from trigonal to tetrahedral. To our knowledge, this is the first observation of an abrupt polyamorphic transition in a three-coordinated glass. Establishing the ubiquity of this process requires further exploration of such materials.

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