

Nature of the Structural Transformations in B₂O₃ Glass under High Pressure

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We study high-pressure polyamorphism of B₂O₃ glass using x-ray diffraction up to 10 GPa in the 300–700 K temperature range, *in situ* volumetric measurements up to 9 GPa, and first-principles simulations. Under pressure, glass undergoes two-stage transformations including a gradual increase of the first B-O (O-B) coordination numbers above 5 GPa. The fraction of boron atoms in the fourfold-coordinated state at $P < 10$ GPa is smaller than was assumed from inelastic x-ray scattering spectroscopy data, but is considerably larger than was previously suggested by the classical molecular dynamics simulations. The observed transformations under both compression and decompression are broad in hydrostatic conditions. On the basis of *ab initio* results, we also predict one more transformation to a superdense phase, in which B atoms are sixfold coordinated.

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Atomic rearrangements and phase transformations in glasses under high pressure and temperature (polyamorphism) are one of the most intriguing and puzzling topics of physics [1–3].

B₂O₃ represents an archetypical oxide glass alongside such glasses as SiO₂ and GeO₂ [4], with the important difference that at the ambient conditions, the structural units are planar BO₃ triangles as opposed to tetrahedra.

As it was found long ago [5,6], the pressure-treated B₂O₃ glass shows residual densification $\Delta\rho/\rho \sim 5\%–10\%$, depending on the pressure-temperature conditions of treatment. The *ex situ* studies of densified glasses point to the breakup of the boroxol rings in the glass structure and to the buckling of the “ribbons” formed by the BO₃ triangles, without any significant coordination change of the boron and oxygen atoms [7,8].

The *in situ* investigations of B₂O₃ glass under pressure have been performed by using Raman and Brillouin spectroscopies [9–11], and through inelastic x-ray scattering spectroscopy [12]. In addition, there have been attempts to examine the B₂O₃ glass under pressure by molecular dynamics simulations, using empirical interatomic potentials [13,14]. According to the data of [9], B₂O₃ glass under compression experiences a transformation in the pressure range $P \sim 6–15$ GPa, with the reverse transformation on decompression occurring sharply at $P \sim 3$ GPa. According to Ref. [12], B₂O₃ glass under pressure features a considerable change in the bonding type in the 6–20 GPa pressure range. These changes were attributed to the modification of the glass short-range order, with the coordination of boron atoms increasing from 3 to 4 in a similar way to crystalline phases.

In view of the current interest in the behavior of B₂O₃ glass under pressure, it is important to carry out direct

in situ experiments, which, in part, has stimulated this work. In this Letter, we report the results of the *in situ* diffraction experiments, *in situ* volumetric measurements, and complement them with the data from *ab initio* calculations.

For the structural study, the dehydrated glassy samples were 2 mm diam, 1 mm high. The *in situ* structural investigations were carried out by the energy-dispersive x-ray diffraction method in the SMAP180 press at the SPring-8 synchrotron radiation facility at the BL14B1 beamline. The spectra were registered at 10 different diffraction angles 2θ from 3° to 24°. A few independent sets of experiments at different temperatures (300–700 K) at 14–16 pressure points in each experiment were carried out.

The *in situ* volumetric measurements of the B₂O₃ glass were conducted by using the toroid high-pressure apparatus. The strain gauge technique [15] was used to measure the sample size. The sample of the B₂O₃ glass 3 mm in size was covered with protective lacquer and placed into a pure hydrostatic high-pressure medium (ethanol-methanol mixture at pressures up to 9 GPa, pentan-isopentan mixture at pressures up to 5.6 GPa). The pressure was continuously monitored by the manganin gauge. The absolute accuracy of the volume measurements was 0.1%, the relative accuracy (measurement sensitivity) was about $10^{-3}\%$.

In the simulation, we used empirical interatomic potentials [16] to equilibrate the 135-atom liquid at 5000 K for 1 ns. The obtained liquid structure was relaxed in the *ab initio* simulation. We have used the SIESTA method [17]. The DZP-basis set was optimized by minimizing the energy of a boroxol molecule capped by hydrogens [18]. Similar to the previous *ab initio* study [19], we obtained the glass structure by quenching the liquid to room temperature. Quenching the liquid and relaxing the resulting struc-

ture produced glass with density 1.9 g cm^{-3} . This structure was used in high-pressure *ab initio* simulations. Each pressure point was simulated for 3–4 ps on Cambridge HPC.

The *in situ* diffraction structural data for the B_2O_3 glass at different pressures are presented in Fig. 1. The structural factor [Fig. 1(b)] smoothly modifies during compression, and at $P > 5\text{--}6 \text{ GPa}$ the structural changes become more pronounced. One can see [Fig. 1(c)] that at $P < 5 \text{ GPa}$, the 1st peak of the total correlation function does not change. The basic changes take place in the distant coordination spheres. At higher pressures the structural changes begin affecting the 1st coordination sphere (see the inset in Fig. 1(c)): the area under the 1st peak expands and the distance in the first sphere slightly increases (conditionally this is a second stage of the transformation). Since the 1st peak corresponds only to the nearest neighbors B-O, the area under the peak is proportional to the coordination number. The calculated coordination number smoothly rises: the fraction of the fourfold-coordination boron atoms can be assessed as being about 15% at $P \sim 8 \text{ GPa}$, $T \sim 300 \text{ K}$; about 30% at $P \sim 9.5 \text{ GPa}$, $T \sim 300 \text{ K}$, and about 45% at $P \sim 9.5 \text{ GPa}$, $T \sim 650 \text{ K}$.

Glass structures under pressure from *ab initio* simulations are shown in Fig. 2. The initial glass structure consists of corner-shared BO_3 triangles [Fig. 2(a)]. At high pressures glass structure consists mostly of BO_4 tetrahedra [Fig. 2(b) and 2(c)]. In Fig. 1(d) we compare the structural correlation function obtained in the experiment and first-principle simulations and observe a reasonable agreement between them, enabling us to qualitatively interpret the experimental data.

At the initial stage of the coordination transformation ($P \sim 5\text{--}7 \text{ GPa}$), there is a slight shift of the B-O average distance whereas the fraction of the fourfold-coordinated boron is close to zero. One can suppose that it is associated with the distortion of BO_3 triangles. The *ab initio* simulations indeed show that before B atoms transform into the fourfold coordination, BO_3 triangles loose their planarity, as the B atom is pushed out of the plane of three O atoms starting from 4–5 GPa [Fig. 2(d)].

According to the structural study, the transformation has significant kinetic effects and greatly accelerates on heating. The reverse structural transformation on decompression occurs in the narrow pressure range of 1–3 GPa. At $P \sim 1.5 \text{ GPa}$, a jumplike behavior is observed, and will be discussed below. The elevated temperature promotes both direct and reverse transformations.

The data of the volumetric measurements are presented in Fig. 3. We have chosen two maxima of pressures, 9 GPa and 5.6 GPa, for two experimental runs, respectively. In this way, the experimental run I corresponds to partial boron-oxygen coordination changes, whereas the experimental run II revealed structural changes happening only in distant coordination spheres. Both runs perfectly agree in the compression stages of the experiments, meaning the absolute reliability of the obtained data (especially noting that these runs were carried out in different liquid hydro-

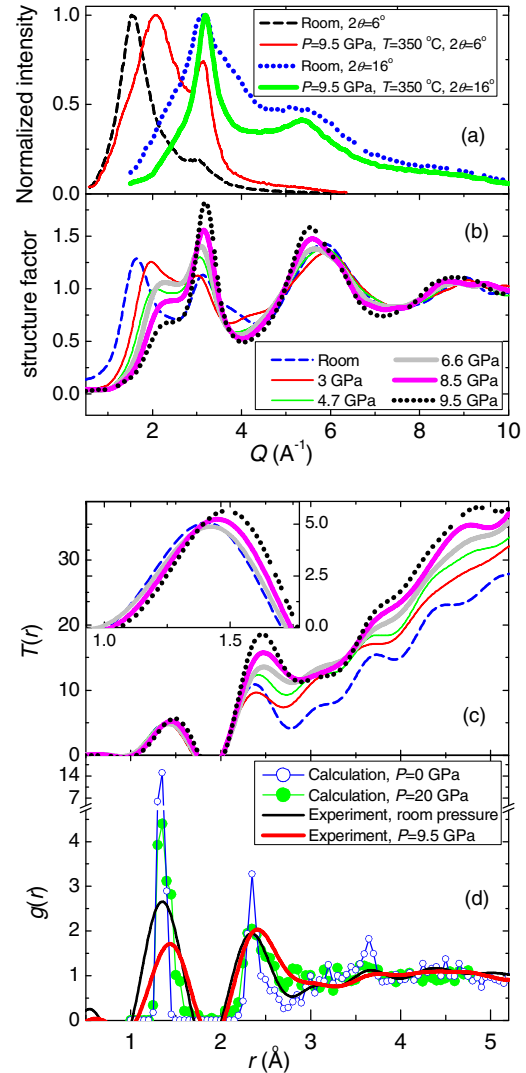


FIG. 1 (color online). Examples of the energy-dispersive x-ray diffraction (EDXD) data for the glassy B_2O_3 (a), measured at different pressures at the two angles of the detector; calculated from the experimental EDXD data structure factor (b) and total correlation function $T(r)$ (c), and comparison of the experimental and computer simulated structural correlation functions $g(r)$ for different pressures (d). All experimental curves for $P = 9.5 \text{ GPa}$ correspond to the sample obtained after heating to 650 K. The line type notations in (c) and in the inset of (c) are the same as in (b). The inset in (c) shows enlarged fragments of selected $T(r)$ curves for the first B-O and O-B coordination spheres. Thicker lines in (b) and (c) correspond to the second stage of the glass transformation.

static mediums). At pressures higher than 2 GPa, an appreciable time-dependent density relaxation is observed in both runs.

The “relaxed” bulk modulus [Fig. 3(b)] at the compression stage is several times smaller than the “unrelaxed” bulk modulus from the data of Ref. [9], suggesting the presence of broad transformation. The bulk modulus does not increase monotonically, changing the slope at $P > 1 \text{ GPa}$ and $P > 5 \text{ GPa}$. One can propose that the trans-

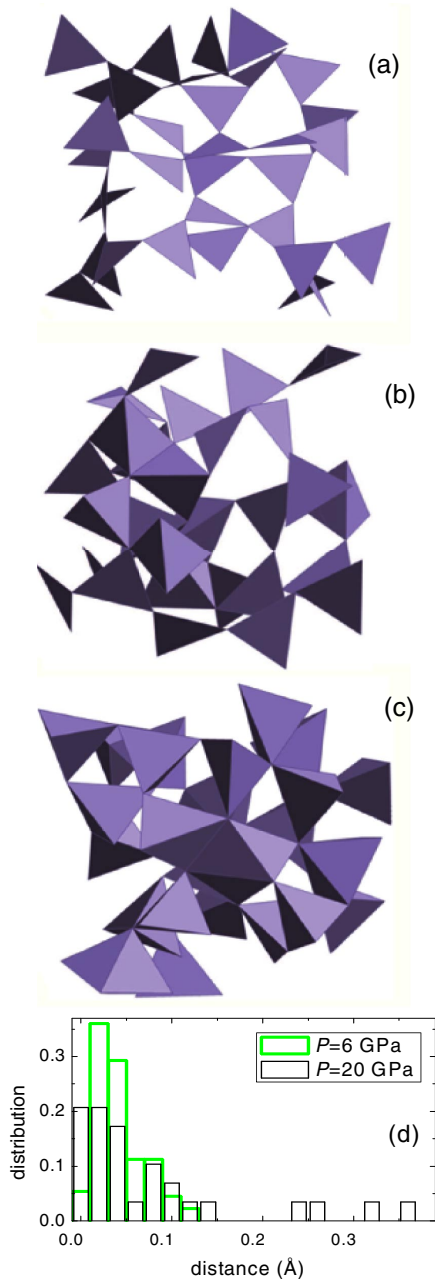


FIG. 2 (color online). Polyhedron representation of the simulated B₂O₃ glass structure at zero pressure (a), $P = 20$ GPa (b), and $P = 200$ GPa (c). The plot (d) shows the distribution of distances from the B atom to the O₃ plane in the BO₃ units for 2 different pressures.

formation in the B₂O₃ glass consists of two broad overlapping transitions occurring at $P > 1$ GPa and $P > 5$ GPa. It is evident that the 1st transformation corresponds to the structural changes in the distant coordination spheres, while the 2nd one at $P > 5$ GPa conforms to the coordination transformation in glass. The initial value of the calculated bulk modulus during the onset of decompression at maximum pressures $B \sim 110$ GPa [Fig. 3(b)] is bound to be equal to the unrelaxed values from [9].

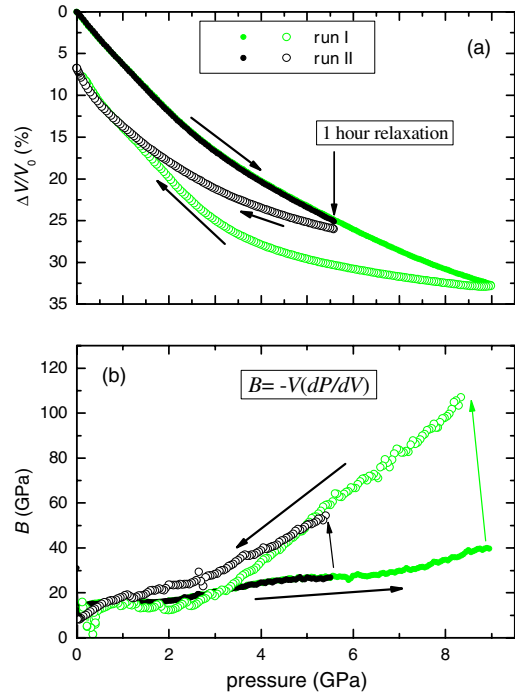


FIG. 3 (color online). Results of the *in situ* volumetric measurements of the glassy B₂O₃ under pressure (a) in the two different runs of compression (solid symbols) and decompression (open symbols), and pressure dependences of the bulk modulus (b) obtained by the direct numerical differentiation of the curves from the plot (a) (relaxed modulus). The significant jumps of the bulk modulus between the final of compression and onset of decompression for both runs correspond to the jumps between relaxed and unrelaxed values (see the text).

The densification after decompression is virtually the same ($\Delta\rho/\rho \sim 6\%$) for both runs [see Fig. 3(a)]. Therefore, the densification is related to the changes in distant coordination spheres. The coordination transition in the 1st sphere is fully reversible. The distinction in the behavior of the relaxed modulus for the two experimental runs during decompression [Fig. 3(b)] is related with the reverse coordination change in glass after 9 GPa treatment. It can be inferred that the decrease of the coordination of the boron atoms from 4 to 3 begins at $P \sim 4.5$ GPa and ends at $P \sim 1$ GPa. The reverse transformation is absolutely smooth in hydrostatic conditions. Therefore, the conclusion made in Ref. [9] about the first-order character of this reverse transition is incompatible with our findings. The volumetric study conducted in the present work involved purely hydrostatic high-pressure conditions. The abrupt changes of sound velocities, observed in Ref. [9], are likely to be an artifact associated with strongly nonhydrostatic conditions near the sample. A similar artifact, related to nonhydrostatic stresses, is the jumplike change of the structure during decompression around 1.5 GPa, which we observed in our structural study.

Figure 4 presents the comparison of the experimental and calculated density and coordination changes with pressure. A reasonable agreement between the experiment

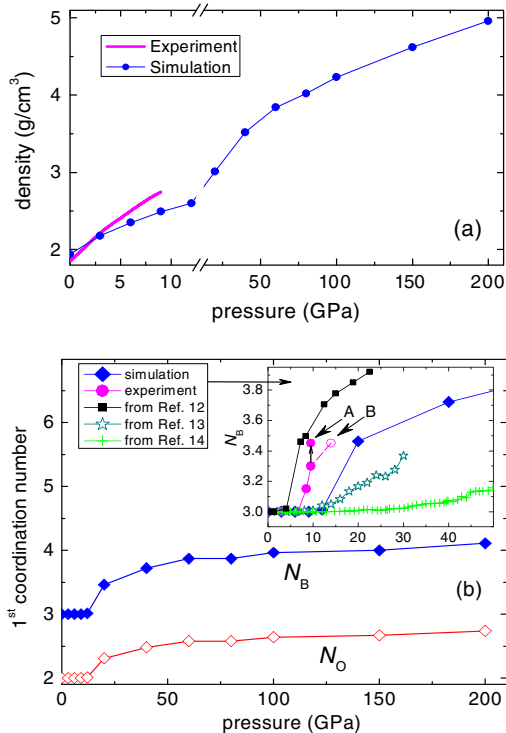


FIG. 4 (color online). Comparison of pressure dependences of the experimental Fig. 3, compression in the run I) and simulated density (a), and simulated pressure dependences of the averaged 1st coordination numbers for B and O (b). The inset in (b) shows pressure dependences of the 1st coordination number for B from the current experiment (x-ray diffraction) and simulation and according to the data from Refs. [12–14]. Point A in the experimental dependence corresponds to the sample state after heating to 650 K under pressure, whereas the open circle (point B) corresponds to the similar state as point A (estimation) which should be observed under room-temperature compression.

and first-principles calculations can be seen. Compared with the experiment, the previous simulations with empirical potentials significantly underestimated the fraction of increased coordination, especially the results from Ref. [14], whereas indirect inelastic x-ray scattering data [12] overestimated the coordination changes under compression [Fig. 4(b)].

The first-principles simulations enable us to analyze the behavior of glass at much larger pressures than those available in the experiments that use large volume presses. We observe that BO_4 tetrahedra at high pressure can be connected in edges [see Fig. 2(b)]. The fraction of edge-shared tetrahedra increases with density, and under further compression face-shared tetrahedra with five- and sixfold-coordinated B atoms appear [Fig. 2(c)].

The behavior of B_2O_3 glass under pressure is in a certain sense similar to the behavior of $\alpha\text{-SiO}_2$. Under pressure, this glass equally features two overlapping diffuse transformations [20]. The 1st transformation is irreversible at room temperature with small change in the coordination,

the second one is reversible; it occurs at higher pressures and is accompanied by the change in the coordination of the Si atoms to 6.

In summary, we presented the results of the first direct *in situ* x-ray experiments and *in situ* volumetric study of B_2O_3 glass under pressure. Combined with *ab initio* simulations, these results allowed us to elucidate the nature of pressure-induced structural changes in this glass. The prediction of our *ab initio* simulations of the transition to the state with sixfold-coordinated B atoms can stimulate the search for the new forms of B_2O_3 with the high coordination under megabar pressures. Such ultradense phases may possibly be quenchable, and should possess very high hardness and elastic moduli.

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