PHYSICAL REVIEW B **78**, 172102 (2008)

First-principles calculations of structural changes in B_2O_3 glass under pressure

K. Trachenko,[1] V. V. Brazhkin,[2] G. Ferlat,[3] M. T. Dove,[1] and Emilio Artacho[1,4]
[1]*Department of Earth Sciences, University of Cambridge, Downing Street, Cambridge, CB2 3EQ, United Kingdom*
[2]*Institute for High Pressure Physics, Troitsk 142190, Russia*
[3]*IMPMC, CNRS-IPGP-Universités Paris 6 et 7, 140 rue de Lourmel, Paris, France*
[4]*Donostia International Physics Center, Paseo Manuel de Lardizabal 4, 20018 San Sebastian, Spain*

(Received 4 August 2008; revised manuscript received 10 October 2008; published 6 November 2008)

Using first-principles calculations, we study pressure effects in B_2O_3 glass up to 600 GPa and perform a detailed analysis of the densified structure. Below approximately 10 GPa, the glass structure deforms without the appearance of increased coordination numbers. At the same time, some of the BO_3 units lose planarity. At higher pressure, we find a gradual increase in fourfold coordinated B atoms. Above approximately 150 GPa, BO_5 and BO_6 polyhedra appear in the structure, and their proportion increases up to the highest studied pressure of 600 GPa. We propose that our analysis stimulate the search for high-density phases of B_2O_3.

DOI: 10.1103/PhysRevB.78.172102 PACS number(s): 61.43.Fs, 62.50.−p

Unlike in crystals, the effects of pressure in amorphous solids are not well understood.[1] Some of the distinct features of high-pressure behavior in amorphous solids include gradual coordination changes, long tails of transformations, slow logarithmic relaxation, permanent densification on pressure release, and others. Several specific terms have been introduced in the area to describe these effects, such as "amorphous-amorphous transformation" and "low- and high-density amorphs," and the possibility of phase transitions between them has been heavily studied and discussed.[1] Generally, it is interesting to understand how the presence of topological disorder gives rise to new effects under pressure.

In addition to being technologically important, B_2O_3 glass is intriguing because its structure differs from most other glasses: the constituent units are planar BO_3 triangles. This makes it unusual as compared to other common glasses with three-dimensional units as SiO_4 tetrahedra in SiO_2 glass. Pressure effects have been studied in B_2O_3 glass in a number of experiments.[2–5] At low pressure, the induced changes are mostly buckling of the network of BO_3 triangles and disappearance of the boroxol rings (see below).[2–4] High-pressure results in the appearance of increased coordinations.[5]

Direct volumetric and *in situ* x-ray measurements of B_2O_3 glass under pressure have recently been reported.[6] In order to understand pressure-induced changes at the microscopic level, it is important to compare these results with those of computer modeling. Molecular-dynamics (MD) simulations with empirical potentials have been used to model pressure effects in B_2O_3 glass.[7,8] Due to the unusual chemistry of this glass, empirical potentials were complex, and included three-body terms and coordination dependence. Despite the elaborate nature of the empirical potentials, their success has been limited: the number of pressure-induced increased coordinations in the simulation[8] is significantly smaller than estimated in the previous indirect inelastic x-ray experiments[5] (see below for more details). Recently, we started to explore what insights can be obtained from the first-principles simulations, and used the results to support the *in situ* experimental studies.[6]

In this Brief Report, we perform high-pressure *ab initio* MD simulations of B_2O_3 glass up to 600 GPa and carry out a detailed analysis of structural changes under pressure. Below approximately 10 GPa, glass structure deforms without the appearance of increased coordination numbers. At the same time, some of the BO_3 units lose planarity. At higher pressure, we find a gradual increase in fourfold coordinated B atoms. Above about 150 GPa, BO_5 and BO_6 polyhedra appear in the structure, and their proportion increases up to the highest simulated pressure of 600 GPa. We propose that our analysis stimulate the search for high-density phases of B_2O_3.

We used empirical interatomic potentials[9] to equilibrate a 135-atom liquid at 5000 K for 1 ns. We then used the *ab initio* MD simulation to relax the liquid and to cool it down to obtain glass. We used the SIESTA method,[10] an implementation of density-functional theory, and employed the Perdew-Burke-Ernzerhof (PBE) generalized gradient approximation to the exchange-correlation energy[11] with norm-conserving pseudopotentials.[12] The Kohn-Sham eigenstates were expanded in a localized basis set of numerical atomic orbitals. The double zeta plus polarization (DZP)-like basis set was optimized by minimizing the energy of a boroxol molecule capped by hydrogens.[13] Similar to the previous study,[14] the liquid was quenched, during about 1 ps, to 300 K to obtain glass and the resulting structure was relaxed. This produced glass with density of about 1.9 g/cm^3, in a reasonably good agreement with the experimental value of 1.8 g/cm^3. This structure was used in high-pressure *ab initio* simulations at 300 K. Each pressure point was simulated for 3–4 ps on Cambridge high-performance computing cluster (HPC). We note that small 135-atom system size is due to computational cost in *ab initio* simulations. It is sufficiently large, however, to study structural modifications in the short range (at distances smaller than 3 Å) below.

The initial glass structure consists of corner-shared BO_3 triangles [see Fig. 1(a)]. A notable feature of B_2O_3 glass is the boroxol ring, consisting of three connected triangles. The exact proportion of these rings has been discussed (for review, see, e.g., Ref. 8). Although, similar to the previous study,[14] we detect a small proportion of these rings (6%), we note that they are not important for the present high-pressure study: it has been shown experimentally[3,4] and in the simulations[7,8] that the boroxol rings disappear under pressure.

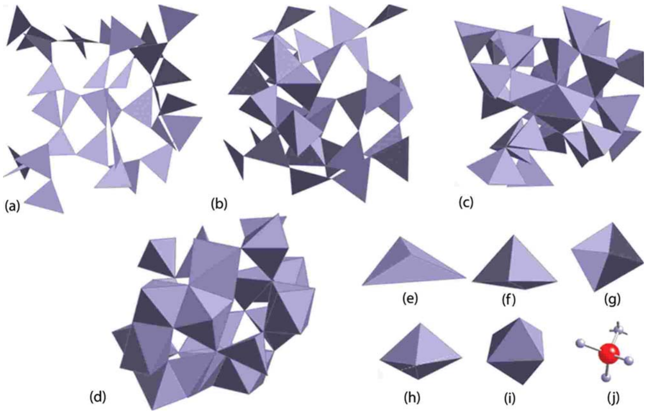

FIG. 1. (Color online) Glass structure at (a) zero pressure, (b) 20 GPa, (c) 200 GPa, and (d) 600 GPa. (e) is a distorted BO_3 unit at 20 GPa. The following elements of glass at $P > 150$ GPa are also shown: (f) five-coordinated BO_5 pyramid with a nearly flat base; (g) same as (f) with a different orientation; (h) BO_5 polyhedron; (i) BO_6 polyhedron; (j) fourfold coordinated O atom. Images generated using CrystalMaker® by CrystalMaker Software Ltd. (www.crystalmaker.com).

In Fig. 2 we plot density under pressure in both experiment[6] and simulation. A reasonable agreement is seen in the low-pressure region, within 8% of difference at the point of maximal deviation. In the inset of Fig. 2 we also plot the results from the previous simulations with empirical potentials.[7,8] We observe that simulations generally underestimate compressibility although *ab initio* results agree better with the experiment.

In Fig. 3 we plot the coordination numbers of B and O atoms. Starting from about 10 GPa, increased coordinations: fourfold coordinated B and threefold coordinated O atoms, appear in the structure. This interestingly compares with SiO_2 glass, where compression is accommodated by the buckling of rigid SiO_4 units until 3 GPa only, after which rebonding kicks in and increased coordinations appear.[15] In the inset of Fig. 3, we compare the simulation results with our recent *in situ* x-ray experiments, in which we calculated B coordination numbers from the area below the first peak in the radial distribution function.[6] A reasonable agreement can be seen; the difference between the experiment and the simulations is partly due to the difference in time scales: our recent experiments show significant time-dependent relaxation processes.[6] We observe that the previous MD simulations with empirical potentials significantly underestimate the number of increased coordinations, in particular the results from Ref. 8. We also note that, compared with the *in situ* x-ray experiments,[6] the previous indirect inelastic x-ray results[5] overestimate the number of increased coordinations.

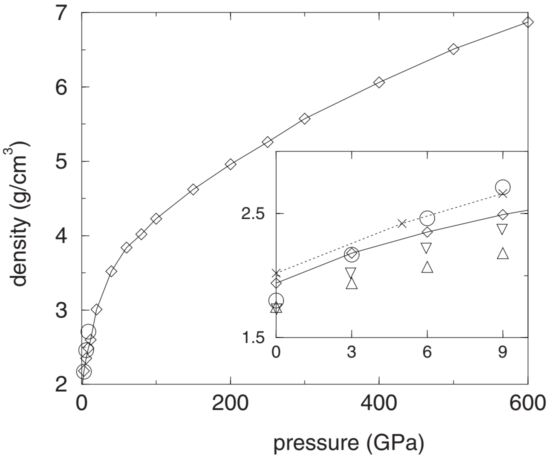

FIG. 2. Experimental (circles) and simulated (solid line) density as a function of pressure. The inset magnifies the low-pressure region, and includes previous MD results with empirical potentials: △,[8] ▽.[7] Crosses ×, joined by the dotted line, show simulated density obtained by sequential decompression from 20 GPa.

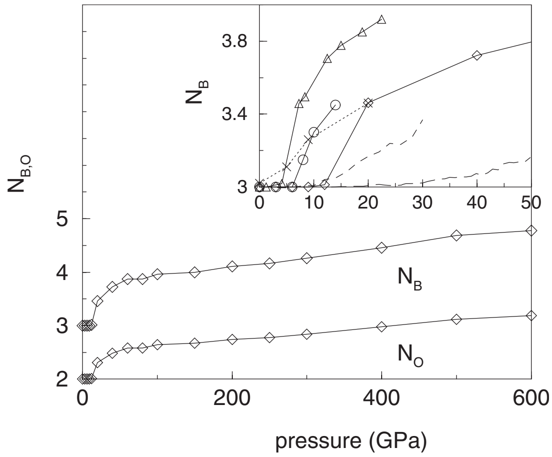

FIG. 3. Average coordination number of B, N_B, (top) and O, N_O, (bottom) atoms as a function of pressure. The inset magnifies the low-pressure region and compares the current *ab initio* results (◇) with our recent x-ray diffraction experiments[6] (○), previous inelastic x-ray scattering experiments[5] (△), and previous MD simulations with empirical potentials from Refs. 7 (dashed line) and 8 (long-dashed line). Crosses ×, joined by the dotted line, show simulated N_B obtained by sequential decompression from 20 GPa.

Unlike their counterparts in silica at room pressure, BO_4 tetrahedra can be connected in edges [see Fig. 1(b)]. This interestingly compares to the recently discovered high-pressure borate crystal, in which BO_4 tetrahedra are both corner and edge sharing.[16] Another difference with the tetrahedral silica structure is that BO_4 tetrahedra are highly distorted from being perfect, as witnessed by the large deviation of O-O-O angles in the faces from 60° (see Fig. 4). As pressure increases, the degree of tetrahedral distortion increases, as witnessed by the wider distribution in Fig. 4.

Our analysis of the structure shows that before B atoms transform into the fourfold coordinations BO_3 triangles lose their planarity as the B atom is pushed from the plane formed by its three O neighbors [see Fig. 1(e)]. In Fig. 5 we plot the distribution of the distances between the B atom and the oxygen plane in three-coordinated states, and observe that these distances increase with pressure, reaching 0.3–0.4 Å at high pressure. It is interesting to note that our recent *in situ* x-ray study shows that at low pressure the first peak of the radial distribution function widens although the area below the peak does not change, i.e., B coordination number does not increase.[6] This can be explained by the distortion of the BO_3 unit from planarity (see also below).

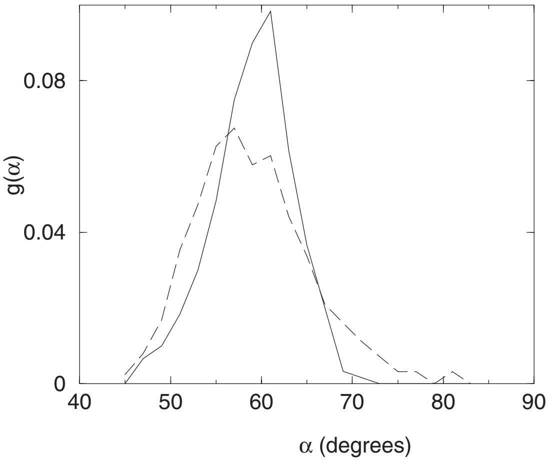

FIG. 4. Distribution of O-O-O angles in BO_4 tetrahedra at 20 (solid line) and 100 GPa (dashed line).

In Fig. 6(a), we compare the radial distribution function calculated at zero and high pressure, and observe that structural changes under pressure are accompanied by the broadening of the B-O and O-O peaks. This is consistent with our recent *in situ* x-ray experiments.[6] To understand the origin of this broadening, we compare the distribution of B-O and O-O distances in BO_3 triangles and BO_4 tetrahedra at zero and high pressures [see Fig. 6(b) and 6(c)]. We observe that the broadening of the B-O and O-O peaks in Fig. 6(a) is primarily due to the increase in B-O and O-O distances in BO_4 tetrahedra. At the same time, the broadening of B-O and O-O distances in three-coordinated states is noticeable, and is related to the deformation of BO_3 triangles from planarity, as discussed above.

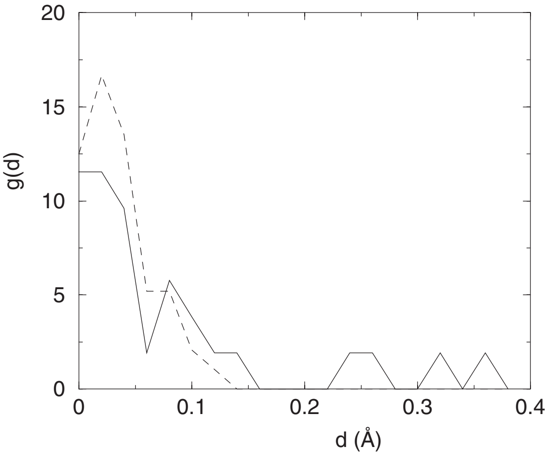

FIG. 5. Distribution of distance *d* from B atom to the O3 plane in the three-coordinated BO_3 states. Solid and dashed lines correspond to 20 and 6 GPa, respectively.

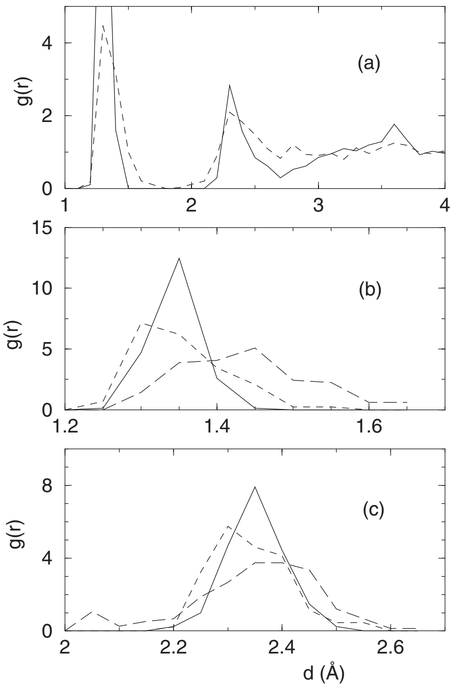

FIG. 6. (a) Total radial distribution function in glass at zero pressure (solid line) and 20 GPa (dashed line); (b) distribution of B-O distances in BO_3 triangles at zero pressure (solid line), in BO_3 triangles (dashed line), and BO_4 tetrahedra (long-dashed line) at 20 GPa; (c) distribution of O-O distances in BO_3 triangles at zero pressure (solid line), in BO_3 triangles (dashed line), and BO_4 tetrahedra (long-dashed line) at 20 GPa. Distributions in (b) and (c) have the area of unity.

To study the effects of remaining densification, we performed decompression along the sequence 20 GPa →9 GPa→5 GPa→0 GPa for about 10 ps. We find a small amount (5%) of densification on decompression (see Fig. 2), consistent with the experimental results.[6] Similarly, the coordination numbers are nearly nonquenchable on decompression although their decrease takes place with a hysteresis (see Fig. 3). These simulations, therefore, predict that high-coordinated glass is not quenchable. This is in contrast to the crystalline form of B_2O_3.[17] We note that the degree of permanent densification in B_2O_3 glass is smaller than in other common glasses: for example, SiO_2 glass shows about 20% of permanent densification on decompression.[15]

We now discuss structural modifications under very high pressure. Starting from 150 GPa, we find fivefold and sixfold coordinated B atoms (see Fig. 1). Up to the highest simulated pressure of 600 GPa, the densified glass is a mixture of tetrahedra and an increasing number of five- and six-corner polyhedra. This is reflected in the gradually increasing coordination numbers in Fig. 3. Fivefold coordinated polyhedra can be seen as either a pyramid with a nearly flat base or as a five-corner irregular polyhedron. This is shown in Fig. 1, together with six-coordinated states. As pressure increases, the number of edge sharing four-, five-, and six-corner polyhedra increases. In this pressure range, we also find fourfold coordinated O atoms (see Fig. 1). We note that *in situ* densification slightly increases at high temperature, suggesting a temperature-dependent transformation; this follows from the simulation at 200 GPa and 1000 K.

These high-coordinated states have not been seen experimentally. High-pressure studies of B_2O_3 crystals have been done only up to 40 GPa.[18] The pressures at which we find high-coordinated states, in which B atom is five or six coordinated and O atom three or four coordinated, are experimentally challenging although achievable in the diamond-anvil cell experiments (200–400 GPa). Given the continuing interest in the high-pressure behavior of B_2O_3,[2–8,16–18] we suggest that our analysis can stimulate the experimental search for high-density phases of B_2O_3, amorphous and crystalline. If high-density crystalline phases are quenchable, as is the tetrahedral B_2O_3 crystal, they would be extremely hard.

In summary, we performed high-pressure *ab initio* simulations of B_2O_3 glass and analyzed its pressure response up to 600 GPa. We proposed that our analysis stimulate the search for high-density phases of B_2O_3.

We are grateful to O. B. Tsiok and Y. Katayama for discussions, and to EPSRC-GB, Royal Society, and RFBR for support.

---

[1] V. V. Brazhkin and A. G. Lyapin, J. Phys.: Condens. Matter **15**, 6059 (2003), and references therein.

[2] E. Chason and F. Spaepen, J. Appl. Phys. **64**, 4435 (1988).

[3] M. Grimsditch, A. Polian, and A. C. Wright, Phys. Rev. B **54**, 152 (1996).

[4] A. C. Wright, C. E. Stone, R. N. Sinclair, N. Umesaki, N. Kitamura, K. Ura, N. Ohtori, and A. C. Hannon, Phys. Chem. Glasses **41**, 296 (2000).

[5] S. K. Lee, P. J. Eng, H. K. Mao, Y. Meng, M. Newville, M. Y. Hu, and J. F. Shu, Nature Mater. **4**, 851 (2005).

[6] V. V. Brazhkin, Y. Katayama, K. Trachenko, O. B. Tsiok, A. G. Lyapin, E. Artacho, M. T. Dove, G. Ferlat, Y. Inamura, and H. Saitoh, Phys. Rev. Lett. **101**, 035702 (2008).

[7] A. Takada, Phys. Chem. Glasses **45**, 156 (2004).

[8] L. Huang, J. Nicholas, J. Kieffer, and J. Bass, J. Phys.: Condens. Matter **20**, 075107 (2008).

[9] Q. Xu, K. Kawamura, and T. Yokokawa, J. Non-Cryst. Solids **104**, 261 (1988).

[10] P. Ordejon, E. Artacho, and J. M. Soler, Phys. Rev. B **53**, R10441 (1996); J. M. Soler, E. Artacho, J. D. Gale, A. Garcia, J. Junquera, P. Ordejon, and D. Sanchez-Portal, J. Phys.: Condens. Matter **14**, 2745 (2002).

[11] J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996).

[12] N. Troullier and J. L. Martins, Phys. Rev. B **43**, 1993 (1991).

[13] G. Ferlat, L. Cormier, F. Mauri, E. Balan, G. Calas, T. Charpentier, and E. Anglada, Phys. Chem. Glasses **47**, 441 (2006).

[14] P. Umari and A. Pasquarello, Phys. Rev. Lett. **95**, 137401 (2005).

[15] K. Trachenko and M. T. Dove, Phys. Rev. B **67**, 212203 (2003); K. Trachenko, M. T. Dove, V. V. Brazhkin, and F. S. El'kin, Phys. Rev. Lett. **93**, 135502 (2004).

[16] J. S. Knyrim, F. Roessner, S. Jakob, D. Johrendt, I. Kinski, R. Glaum, and H. Huppertz, Angew. Chem., Int. Ed. **46**, 9097 (2007).

[17] C. T. Prewitt and R. D. Shannon, Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem. **24**, 869 (1968); V. V. Brazhkin, Y. Katayama, Y. Inamura, M. V. Kondrin, A. G. Lyapin, S. V. Popova, and R. N. Voloshin, JETP Lett. **78**, 393 (2003).

[18] D. Nieto-Sanz, P. Loubeyre, W. Crichton, and M. Mezouar, Phys. Rev. B **70**, 214108 (2004).