Structural Transformations and Anomalous Viscosity in the B_2O_3 Melt under High Pressure

V. V. Brazhkin,[1,*] I. Farnan,[2] Ken-ichi Funakoshi,[3] M. Kanzaki,[4] Y. Katayama,[5] A. G. Lyapin,[1] and H. Saitoh[5]

[1]*Institute for High Pressure Physics RAS, 142190 Troitsk Moscow region, Russia*
[2]*Department of Earth Sciences, University of Cambridge, Downing Street, Cambridge, CB2 3EQ, United Kingdom*
[3]*Japan Synchrotron Radiation Research Institute (JASRI), SPring-8, 1-1-1 Kuoto, Sayo-cho, Sayo-gun, Hyogo, 679-5198, Japan*
[4]*Institute for Study of the Earth Interior, Okayama University, Yamada 827, Misasa, Tottori 682-0193, Japan*
[5]*Japan Atomic Energy Agency (JAEA), SPring-8, 1-1-1 Kuoto, Sayo-cho, Sayo-gun, Hyogo, 679-5143, Japan*
(Received 22 June 2010; published 9 September 2010)

Liquid B_2O_3 represents an archetypical oxide melt with a superhigh viscosity at the melting temperature. We present the results of the *in situ* x-ray diffraction study and the *in situ* viscosity measurements of liquid B_2O_3 under high pressure up to 8 GPa. Additionally, the ^{11}B solid state NMR spectroscopy study of B_2O_3 glasses quenched from the melt at five different pressures has been carried out. Taken together, the results obtained provide understanding of the nature of structural transformations in liquid B_2O_3. The fraction of the boroxol rings in the melt structure rapidly decreases with pressure. From pressures of about 4.5 GPa, four-coordinated boron states begin to emerge sharply, reaching the fraction 40%–45% at 8 GPa. The viscosity of the B_2O_3 melt along the melting curve drops by 4 orders of magnitude as the pressure increases up to 5.5 GPa and remains unchanged on further pressure increase.

Phase transitions in disordered substances are one of the most intriguing and puzzling areas of physics [1]. Structural transformations in some oxide melts are likely to be responsible for atypical pressure dependences of their viscosities [2–4]. B_2O_3 melt is an archetypical supervis-cous glass-forming liquid, which is anomalous in that its crystallization from the melt at room pressure has never been observed [5]. Both B_2O_3 melt and glass stand out among other oxides, first, because of a unique cation coordination equaling 3, and, second, because both B_2O_3 liquid and glass include a significant fraction of unique structural units—boroxol groups (3-membered rings $B_3O_6{}^{3-}$) (see, e.g., [6]). Research into the behavior of B_2O_3 melt under compression is of extreme importance both to the physics of phase transitions and to the geophysics. The presence of B_2O_3 in magmatic melts could have a significant effect on the dynamics of melts in Earth's interior [7].

The high-pressure behavior of B_2O_3 glass and crystals has been studied previously (see, e.g., [8–13]). The disappearance of the boroxol rings and the passage to four-coordinated boron states under compression have been found. Unlike crystalline phases and glass, the structure and properties of liquid B_2O_3 under pressure have virtually been unexplored earlier. A preliminary study on liquid B_2O_3 structure under pressures $P < 4$ GPa was done in [14]. There was an attempt of an indirect investigation into the structure of B_2O_3 melt by a NMR study of B_2O_3 glass quenched from the melts under two pressures (2 and 6 GPa) [15]. There were also computer simulation studies of liquid B_2O_3 under pressure—using an empirical interatomic potential [16], and *ab initio* study [17]. The predictions were made about the changes in the short-range order structure of liquid B_2O_3 under pressure and about the

acceleration of the diffusion of boron and oxygen ions under pressure along the isotherms (5000 and 2500 K, respectively, in [16,17]).

The present work was aimed at performing experimental research under pressure on the structure and viscosity of liquid B_2O_3. The research has involved *in situ* x-ray diffraction measurements up to 8 GPa and 2000 K, an *in situ* viscosity study by real-time radiography technique up to 7 GPa and 1900 K, and a NMR study of B_2O_3 glasses prepared by quenching from the melts under five different pressures.

The structural investigations of the B_2O_3 melt 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 beam line. The spectra were registered at eight different diffraction angles (from 4° to 18°). Radial distribution function (RDF) $4\pi r^2 \rho(r)$ was calculated from the structural factor $S(Q)$ with damping factor diminishing from 1 down to 0 in the interval 8–12 Å^{-1} of the scattering wave vector.

To measure *in situ* viscosity of B_2O_3 melt we employed a real-time radiography to image the velocity of a sphere falling through the liquid. A double-stage multianvil high-pressure cell installed at BL04B1 beam line was used. Radiography images were collected by means of a high-speed CCD camera. B_2O_3 glass cylinders of 1.5 mm in diameter and 2 mm in height were used. Pt spheres with diameters ranging from 80 to 160 μm were used as viscosity markers. The viscosity values η were calculated through the Stokes equation with the wall and the end corrections [18].

Samples of densified B_2O_3 glasses (2 mm height, 2.5 mm diameter) for ^{11}B solid state NMR spectroscopy study were prepared by rapid quenching from the melt

(1000 K/s cooling rate) using a "toroid" high-pressure apparatus [19] at five different pressures up to 5.8 GPa (at higher pressures the crystallization of the melt is unavoidable even at high cooling rates). We have checked the absence of any crystalline and water impurities in the glasses just before NMR study. We used a Varian Infinity plus NMR spectrometer (11.7 T) operating at 160 MHz for B-11. The spectra analysis has been performed using the DMFIT program [20].

The results of the *in situ* x-ray diffraction study on liquid B_2O_3 are illustrated in Fig. 1. There is anomalous behavior of the pressure dependence of the structure factors near 4–5 GPa [Figs. 1(c) and 1(d)]. A similar discontinuity can be recognized in the pressure dependence of the radius of the 1st coordination sphere [Fig. 1(e)]. Thus, there is experimental evidence for the existence of a pressure-localized structural transformation in the liquid state of B_2O_3 in the interval 4–5 GPa near the melting curve.

The radius of the 1st coordination sphere r_1 in liquid B_2O_3 [Fig. 1(e)] changes from 1.39(6) at 1.2 GPa to 1.45(4) at 8 GPa. This correlates with the pressure dependence of r_1 in glassy B_2O_3 [13] and reflects the corresponding increase in the coordination number N_{B-O}. The variation of r_1 with pressure in liquid B_2O_3 can also be compared with average B-O distances in crystalline low-pressure ($\langle r_{B-O} \rangle = 1.37$ Å) and high-pressure ($\langle r_{B-O} \rangle = 1.47$ Å) phases (see, e.g., Ref. [21]). The area under the RDF for the 1st sphere is $N_1^{RDF} = 1.71$, 1.90, 1.90, and 2.05 for $P = 1.2$, 4.3, 5.7, and 8 GPa, respectively. An increase in N_1^{RDF} between 1.2 and 8 GPa implies an increase in N_{B-O} from 3 to 3.45. This means that up to 40%–45% boron atoms can be fourfold coordinated by oxygen in liquid B_2O_3 at 8 GPa.

Figure 2 shows ^{11}B magic angle spinning (MAS) NMR spectra for B_2O_3 glasses quenched from the melts at varying pressure. The fraction of the boron atoms belonging to the boroxol rings significantly decreases as the pressure rises [see Fig. 2(b)]. In the 3.2–4.7 GPa pressure range, the flattening of the pressure dependence of the fraction of the boroxol rings is observed, and the shape of the NMR spectra changes profoundly. This behavior correlates with an anomalous behavior of the structure parameters at pressures of 4–5 GPa (see Fig. 1). It is obvious that at this pressure interval a considerable distortion of the BO_3 triangles begins, and a simple separation of the states of the boron atoms into two types appears inadequate. The fraction of boroxol rings for low-pressure quenched glasses is in good correspondence with recent estimations [22]. Obviously, some of boroxol groups appear during the quenching process [22], and the corresponding melts contain a lower fraction of the rings than the quenched glasses (see also [6]).

The NMR spectra of the glasses obtained by quenching from the melts at pressures higher than 4.7 GPa reveal a peak corresponding to the tetracoordinated states of the boron atoms. At pressures below 4 GPa, the fourfold
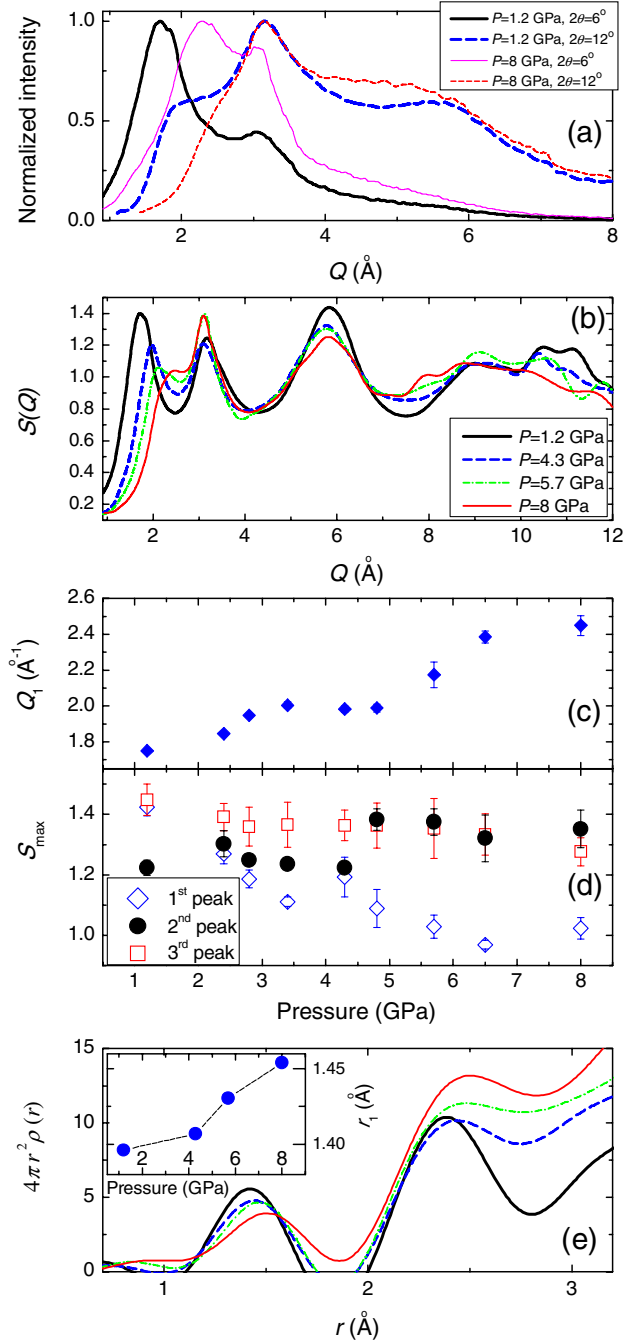

FIG. 1 (color online). Examples of the energy-dispersive x-ray diffraction (EDXD) data for the liquid B_2O_3 under pressure (a) measured at the two angles of the detector and (b) calculated from the experimental EDXD data and smoothed total interference functions for different pressures. (c) Q position of the first peak of the structure factor, (d) amplitudes of the first three maxima of the structure factor, and (e) radial distribution functions [notations are the same as in (b)] of liquid B_2O_3, where the inset shows the pressure dependence of the radius of the 1st coordination sphere.

coordinated boron atoms in the glasses are absent, as indicated by both the structural and the NMR data. The fraction of the fourfold coordinated boron atoms in the glasses obtained at 5.8 GPa is 3%–4%, which is
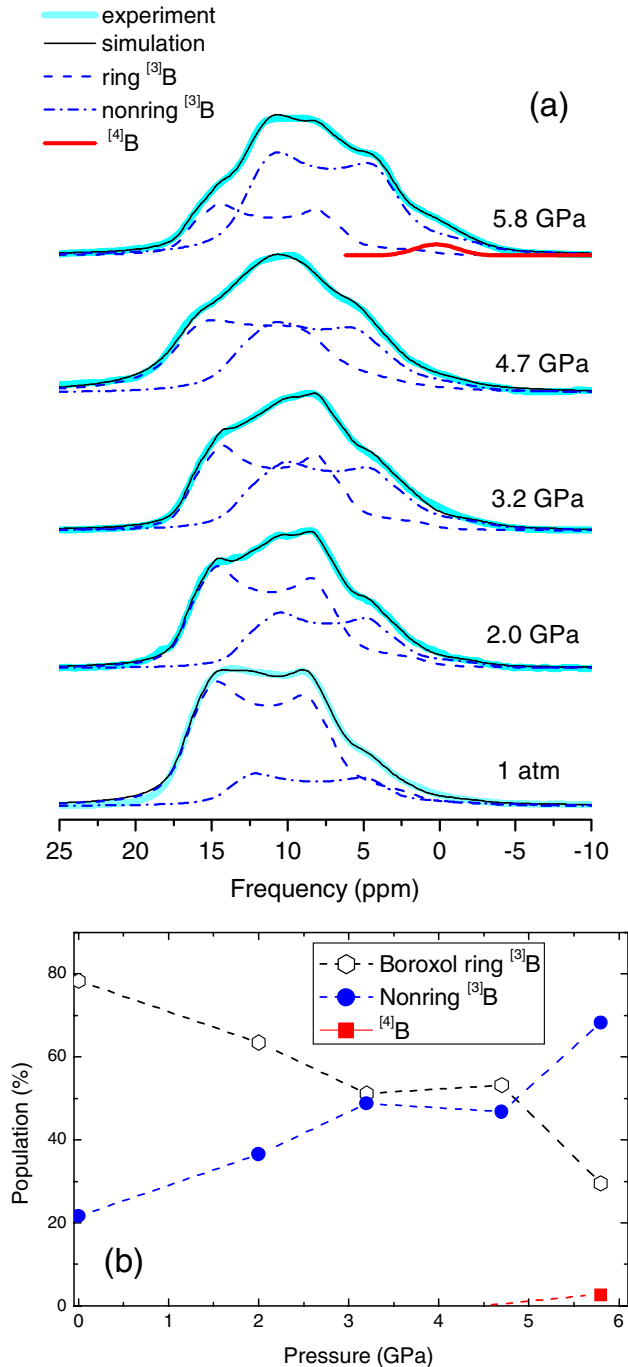
P H Y S I C A L   R E V I E W   L E T T E R S

FIG. 2 (color online). Experimental ^{11}B MAS NMR spectra for B_2O_3 glasses, quenched from the melt at different pressures P_{syn}, and their simulations with decomposition (a) and the population vs P_{syn} dependences for different boron sites (b). The NMR fitting parameters, such as isotropic chemical shift δ_{iso} [ppm], quadrupolar coupling constant C_q [MHz], and quadrupolar asymmetry parameter η, for the boroxol ring $^{[3]}$B and nonring $^{[3]}$B are the following, respectively: 18.3, 2.61, 0.22 and 15.9, 2.76, 0.17 for $P_{syn} = 1$ atm; 18.3, 2.66, 0.22 and 14.5, 2.65, 0.27 for $P_{syn} = 2.0$ GPa; 18.2, 2.67, 0.24 and 14.5, 2.68, 0.32 for $P_{syn} = 3.2$ GPa; 18.8, 2.62, 0.04 and 15.0, 2.62, 0.31 for $P_{syn} = 4.7$ GPa; 18.3, 2.69, 0.23 and 14.5, 2.67, 0.20 for $P_{syn} = 5.8$ GPa. The position of $^{[4]}$B peak for $P_{syn} = 5.8$ GPa is equal 0.2 ppm.

significantly lower than the estimations based on the *in situ* x-ray diffraction data. This disagreement can be due to two reasons. First, when estimating the fraction of the fourfold coordinated boron atoms from the structural data, almost all boron atoms pushed out of the BO_3 triangles are assigned to the 1st coordination sphere, whereas the ^{4}B peak in the NMR spectra arises from almost regular BO_4 tetrahedra. Second, some fraction of the fourfold coordinated states present in the melt may not be retained after quenching and pressure release (see also [13]). The conclusion about high values of the fraction of fourfold coordinated boron atoms in pressure quenched glasses, previously drawn in Ref. [15] from the NMR spectra, seems incorrect; the discrepancy is likely to be due to the presence of the impurity of a high-pressure crystalline phase in the glass obtained at 6 GPa and (or) water impurity in both glasses obtained at 2 and 6 GPa in [15].

Structural changes in B_2O_3 melt under pressure cause cardinal changes in its properties, including the viscosity. The data from the *in situ* viscosity measurements of B_2O_3 melt are shown in Fig. 3. A record 4 orders of magnitude decrease (from 3000 to 0.3 Pa s) in the viscosity along the melting curve with increasing pressure up to 5.5 GPa is observed. On further pressure increase, the viscosity along the melting curve remains virtually unchanged. It is of interest that an additional abrupt decrease in the viscosity along the melting curve takes place at a pressure of about 4 GPa immediately before the fourfold coordinated atoms appear. At the same time, the viscosity ceases to decrease with increasing pressure at $P > 5.5$ GPa, when an appreciable (10%–20%) fraction of the fourfold coordinated boron atoms is already present in the melt. Along the isotherms, the viscosity weakly decreases in the initial pressure range from 0 to 3 GPa (the corresponding temperature range is 800–1300 K) and rapidly decreases in the higher temperature range of 1300–1700 K (pressures from 3 up to 5.5 GPa) [see Fig. 3(a)]. Finally, under pressures exceeding 5.5 GPa, the viscosity on the isotherms rises with pressure.

The *ab initio* molecular dynamics study [17,23] has revealed that the atomic diffusion occurs through the formation of intermediate overcoordinated BO_4 groups and undercoordinated units. At higher pressures, a change in the diffusion mechanism occurs through the appearance of simultaneously two BO_4 overcoordinated groups without undercoordinated ones [17,23]. Finally, at higher pressures, a significant portion of boron atoms is already in the tetracoordinated state and the pressure begins to retard the diffusion due to the cage effect. All abovementioned factors give rise to that complex viscosity behavior. Both previous computer simulation studies of the melt [16,17] have correctly predicted the appearance of four-coordinated boron states under pressure and the increase in diffusion coefficients. Moreover, the maximum diffusion rate (the minimum viscosity) at $P \sim 10$ GPa was foretold in [17]. The absolute values of the fraction of four-coordinated boron states and of diffusivity predicted
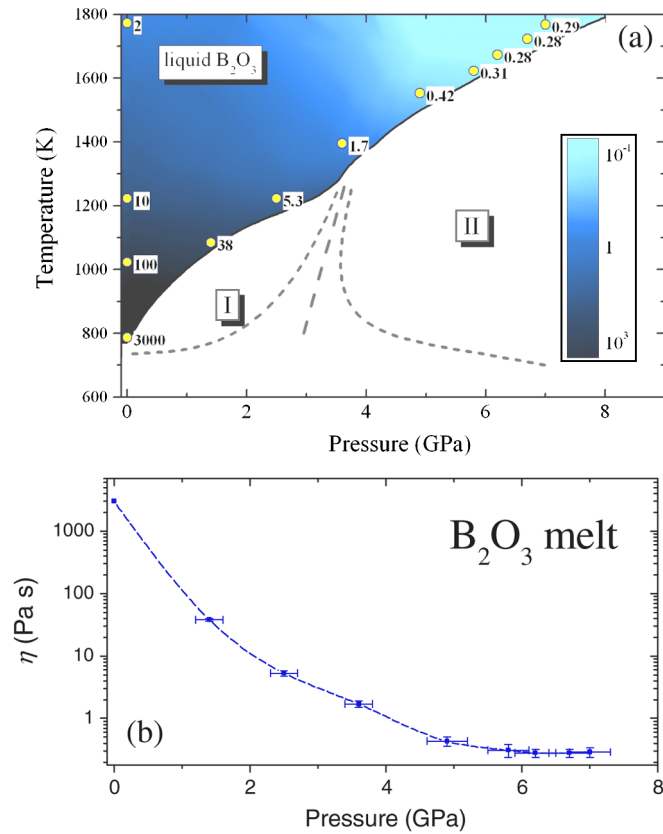
FIG. 3 (color online). Experimental phase diagram of B_2O_3 with the approximated color mapping of the melt viscosity (in Pa s units) (a) and pressure dependence of viscosity along the melting curve (b). The experimental pressure-temperature points, where viscosity was measured, are marked in (a) by the measured values of viscosity.

in [16,17] are difficult to compare with the experimental data because the temperature values used in simulation were significantly higher than the melting temperature.

Thus, B_2O_3 melt is now the first simple oxide liquid whose structure and viscosity have been simultaneously subject to *in situ* studies in a wide pressure range. A considerable modification of the medium- and short-range order in B_2O_3 melts causes a complex nonmonotonic viscosity behavior. The boroxol groups in B_2O_3 melt quickly disappear under pressure. A noticeable fraction of the fourfold coordinated boron atoms appears under pressure $P > 4.5$ GPa. The melt is altered at compression from an ultraviscous to a nonviscous one: at $P > 5.5$ GPa the viscosity of B_2O_3 melt near the melting temperature is close to the viscosity of olive oil. Obviously, "strong" B_2O_3 liquid becomes much more "fragile" under compression. If the crystallization of B_2O_3 melt at room pressure is virtually impossible even on slow cooling, then at higher pressures, by contrast, it cannot practically be prevented even on rapid cooling.

*brazhkin@hppi.troitsk.ru
[1] *New Kinds of Phase Transitions: Transformations in Disordered Substances*, edited by V. V. Brazhkin, S. V. Buldyrev, V. N. Ryzhov, and H. E. Stanley (Kluwer, Dordrecht, 2002).
[2] C. A. Angel, P. A. Cheeseman, and S. Tamaddon, Science **218**, 885 (1982).
[3] P. F. McMillan and M. C. Wilding, J. Non-Cryst. Solids **355**, 722 (2009).
[4] B. B. Karki and L. P. Stixrude, Science **328**, 740 (2010).
[5] D. R. Uhlmann, J. F. Hays, and D. Turnbull, Phys. Chem. Glasses **8**, 1 (1967).
[6] J. Sakowski and G. Herms, J. Non-Cryst. Solids **293-295**, 304 (2001).
[7] D. B. Dingwell, M. Pichavant, and F. Holtz, in *Boron, Mineralogy, Petrology and Geochemistry*, edited by E. S. Grew and L. M. Anovitz (Mineralogical Society of America, Washington, DC, 1996), p. 331.
[8] J. Nicholas *et al.*, Phys. Rev. Lett. **92**, 215701 (2004).
[9] L. P. Huang and J. Kieffer, Phys. Rev. B **74**, 224107 (2006).
[10] L. P. Huang, M. Durandurdu, and J. Kieffer, J. Phys. Chem. C **111**, 13712 (2007).
[11] L. P. Huang *et al.*, J. Phys. Condens. Matter **20**, 075107 (2008).
[12] M. Grimsditch, A. Polian, and A. C. Wright, Phys. Rev. B **54**, 152 (1996).
[13] V. V. Brazhkin *et al.*, Phys. Rev. Lett. **101**, 035702 (2008).
[14] V. V. Brazhkin *et al.*, JETP Lett. **78**, 393 (2003).
[15] S. K. Lee *et al.*, Phys. Rev. Lett. **94**, 165507 (2005).
[16] J. Diefenbacher and P. F. McMillan, J. Phys. Chem. A **105**, 7973 (2001).
[17] S. Ohmura and F. Shimojo, Phys. Rev. B **80**, 020202(R) (2009).
[18] V. V. Brazhkin, M. Kanzaki, Ken-ichi Funakoshi, and Y. Katayama, Phys. Rev. Lett. **102**, 115901 (2009).
[19] L. G. Khvostantsev, V. N. Slesarev, and V. V. Brazhkin, High Press. Res. **24**, 371 (2004).
[20] D. Massiot *et al.*, Magn. Reson. Chem. **40**, 70 (2002).
[21] A. Takada *et al.*, Phys. Rev. B **51**, 1447 (1995).
[22] G. Ferlat *et al.*, Phys. Rev. Lett. **101**, 065504 (2008).
[23] S. Ohmura and F. Shimojo, Phys. Rev. B **78**, 224206 (2008).