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Anomalous pressure dependence of self-diffusion in liquid B_2O_3: An *ab initio* molecular dynamics study

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The pressure dependence of the static and dynamic properties of liquid boron oxide, B_2O_3, is studied by *ab initio* molecular dynamics simulations. Planar BO_3 units are found to be scarcely deformed under pressures up to about 3 GPa. Under further compression, the number of tetrahedral BO_4 units increases gradually, and approximately 90% of boron atoms have fourfold coordination near 100 GPa. The self-diffusion coefficients of boron and oxygen have a maximum at a pressure of about 10 GPa. We find that under pressures above 20 GPa, the diffusivity of boron becomes about two times larger than that of oxygen, while the former is 10–20% smaller than the latter at lower pressures. We reveal the microscopic origin of this anomalous pressure dependence of diffusivity.

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Boron oxide (B_2O_3) is a typical glass-forming oxide and also a technologically important material. In the structures of crystalline and vitreous B_2O_3 in ambient conditions, each boron atom is coordinated to three oxygen atoms with single bonds, forming a triangular BO_3 unit, and each oxygen atom is twofold coordinated to boron atoms.[1,2] Under compression, crystalline B_2O_3 is transformed from the trigonal to the orthorhombic phase at about 6.5 GPa.[3,4] The high-pressure structure consists of interconnected tetrahedral BO_4 units. Although each boron atom bonds to four oxygen atoms, two-thirds of the oxygen atoms are threefold coordinated to boron atoms and the remaining maintain twofold coordination. In vitreous B_2O_3 under pressure, fourfold-coordinated boron atoms appear at approximately 10 GPa,[5,6] and their number increases gradually with increasing pressure.

Upon melting at atmospheric pressure, the local coordination around each atom remains the same.[7] However, unlike in the crystalline and vitreous states, the covalent bonds are rearranged with long-range atomic diffusion in the liquid state. Recent first-principles investigation of the structural and bonding properties of liquid B_2O_3 (Ref. 8) has revealed that under ambient conditions, a nonbridging oxygen double bonded to a twofold-coordinated boron is always involved with atomic diffusion accompanied by rearrangement of the covalent bonds to reduce the formation energy of the overcoordination defects. Concerning the effect of pressure on the liquid state, quenching experiments[9] under pressures of up to 8 GPa have shown that the viscosity of the undercooled melt decreases with increasing pressure. X-ray scattering experiments have been performed for liquid B_2O_3 to investigate the pressure-induced structural change;[10] they suggested the existence of a first-order-like transition to a high-density phase near 7 GPa. The transport properties of liquid B_2O_3 under pressure have been studied by molecular dynamics (MD) simulations using an empirical interatomic potential.[11] The diffusivity of atoms was shown to increase with pressure, as in other covalent liquids, such as SiO_2 and GeO_2.[12,13] It is, however, unclear how the rearrangement process of the covalent bonds is affected by compression. Because the calculated results obtained by empirical potentials depend on the choice of the potential form, theoretical investigations based on first-principles theory would be needed to clarify the microscopic mechanism of atomic diffusion in the liquid state under pressure.

For this purpose, we utilized *ab initio* MD simulations. The electronic states were calculated using the projector-augmented-wave method[14,15] within the framework of density functional theory. The generalized gradient approximation[16] was used for the exchange-correlation energy. The plane-wave cutoff energies are 30 and 200 Ry for the electronic pseudowave functions and the pseudocharge density, respectively. The Γ point was used for Brillouin zone sampling. A system of 120 (48B+72O) atoms in a cubic supercell was used under periodic boundary conditions. The equations of motion for atoms were solved via an explicit reversible integrator[17] with a time step of $\Delta t = 1.2$ fs.

To determine the density of the liquid state under pressure, a constant-pressure MD simulation[18] was performed for 2.4 ps at each given pressure. Using the time-averaged density, the static and diffusion properties were investigated by MD simulations in the canonical ensemble.[19] Seven thermodynamic states used in this study cover a density range from 1.69 to 3.99 g/cm^3 and a pressure range from 1.4 to 97.0 GPa, as listed in Table I. The temperature of 2500 K was chosen so as to be sufficiently high to maintain the liquid state even at the high pressures investigated. The procedure for obtaining the liquid state from the crystalline configuration has been described in a previous paper.[8] The quantities of interest were obtained by averaging over 21.6 ps long enough to achieve good statistics after the initial equilibration, which takes at least 2.4 ps

Figure 1 shows the simulated pressure dependence of the nearest-neighbor distances, $r_{\alpha-\beta}$, which were obtained from the first-peak positions of the pair-distribution functions, $g_{\alpha-\beta}(r)$. No homopolar bonds exist even when the pressure approaches 100 GPa, and $r_{\text{B-O}}$ is much smaller than $r_{\text{B-B}}$ and $r_{\text{O-O}}$. All three $r_{\alpha-\beta}$ have only weak pressure dependence up to about 10 GPa, which implies that the local structure within the first-coordination shell is almost unchanged during compression up to about $V/V_0 = 0.64$. With further compression, $r_{\text{B-O}}$ increases with pressure and has a maximum at about 50 GPa, while $r_{\text{B-B}}$ and $r_{\text{O-O}}$ decrease monotonically, indicating

TABLE I. Densities $\rho(\mathrm{g/cm^3})$ used in MD simulations of liquid B_2O_3 in the canonical ensemble at a temperature of 2500 K. The relative volumes V/V_0, where V_0 is the volume at $\rho=1.50\ \mathrm{g/cm^3}$ ($P=0.0$ GPa), and the time-averaged pressures (Refs. 20 and 21) P(GPa) are also listed.

ρ $(\mathrm{g/cm^3})$	V/V_0	P (GPa)
1.69	0.89	1.4
1.92	0.78	3.2
2.36	0.64	9.2
2.63	0.57	15.5
3.08	0.49	28.4
3.42	0.44	46.2
3.99	0.38	97.0

that the local structure changes greatly with pressure.

To discuss the pressure dependence of the local structure in detail, we show the pressure dependence of the coordination-number distribution $f^{(n)}_{\alpha-\beta}$ in Fig. 2. $f^{(n)}_{\alpha-\beta}$ is the ratio of the number of α-type atoms that are coordinated to $n\beta$-type atoms to the total number of α-type atoms. To obtain $f^{(n)}_{\alpha-\beta}$, we counted the number of β-type atoms inside a sphere with radius R centered at each α-type atom, where $R=1.9$ Å is a cutoff distance determined from the first-minimum position of $g_{\text{B-O}}(r)$ at $\rho=1.69\ \mathrm{g/cm^3}$. Because both $f^{(3)}_{\text{B-O}}$ and $f^{(2)}_{\text{O-B}}$ have high values of about 0.98, i.e., 98% of B and O atoms have threefold and twofold coordinations, respectively, under pressure up to about 3 GPa, liquid B_2O_3 consists mainly of BO_3 units connected by bridging O atoms in this pressure range. With increasing pressure, for $P>3$ GPa, $f^{(3)}_{\text{B-O}}$ and $f^{(2)}_{\text{O-B}}$ decrease, and instead $f^{(4)}_{\text{B-O}}$ and $f^{(3)}_{\text{O-B}}$ increase. This means that the number of BO_4 units increases gradually in the liquid state, as in the vitreous states. While $f^{(3)}_{\text{B-O}}$ and $f^{(4)}_{\text{B-O}}$ are exchanged for each other at about 25 GPa, $f^{(2)}_{\text{O-B}}$ and $f^{(3)}_{\text{O-B}}$ are interchanged at a higher pressure of about 50 GPa because of the composition ratio of B and O atoms. At about 100 GPa, the number of fourfold-coordinated B atoms approaches about 90%, and about 5% of B atoms have fivefold coordination.

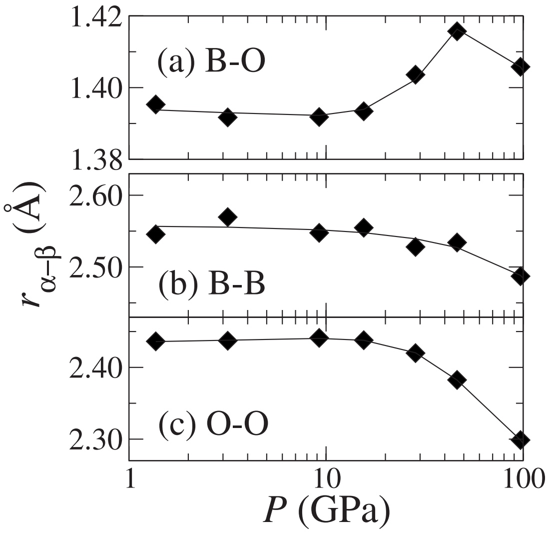

FIG. 1. Pressure dependence of the nearest-neighbor distances $r_{\alpha-\beta}$ for $\alpha-\beta=$(a) B-O, (b) B-B, and (c) O-O.

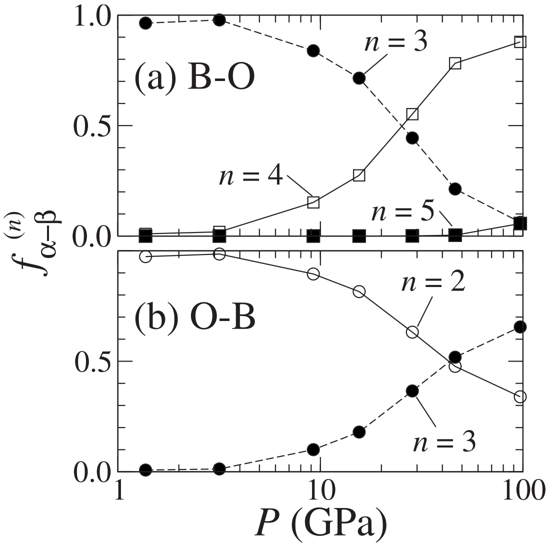

FIG. 2. Pressure dependence of the coordination-number distribution $f^{(n)}_{\alpha-\beta}$ for $\alpha-\beta=$(a) B-O and (b) O-B.

Figure 3 shows the diffusion coefficients D_α for $\alpha=$B and O atoms as a function of pressure. Clearly, liquid B_2O_3 has a diffusion maximum around 10 GPa. In the pressure range of $0<P<10$ GPa, both D_B and D_O show a similar increase with increasing pressure, which is consistent with the observed pressure dependence of the viscosity of the undercooled liquid.[9] The diffusion enhancement is related to a weakening of the covalentlike interaction between atoms accompanying the increase in the coordination number, as in other covalent liquids.[12,13] In fact, we found that in liquid B_2O_3 under pressures above 3 GPa, long-range atomic diffusion occurs by the usual concerted reactions, while the nonbridging O atoms are always involved in diffusion processes at lower pressures.[8] In each concerted reaction, two BO_4 groups are generated as an intermediate by forming two new B-O bonds between adjoining BO_3 units, whereas only one BO_4 group is required to produce one nonbridging O atom.

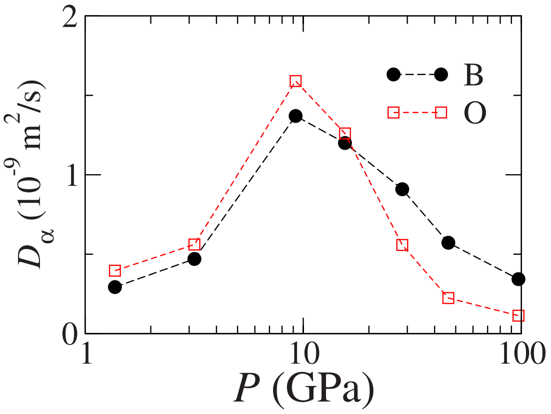

FIG. 3. (Color online) Pressure dependence of the diffusion coefficients D_α for $\alpha=$B (solid circles) and O (open squares) atoms.

The concerted reactions occur more frequently with increasing pressure, which should result from covalent-bond weakening due to compression, and should enhance the atomic diffusion. We also observed that the reactions with the nonbridging O atoms decrease in number with pressure and almost disappear for $P > 10$ GPa.

The concerted reactions as well as those with the nonbridging O atoms involve equal numbers of B and O atoms; therefore, D_B and D_O would show a similar pressure dependence up to about 10 GPa, as seen in Fig. 3. In this lower pressure range, there exists fairly large empty space between atoms, and therefore atoms can diffuse while maintaining the covalent bonds even between the events of bond-exchange reaction. Although such atomic diffusion takes place within a limited distance, O atoms have more freedom to move than B atoms because of their lower-coordination number. This difference may result in the fact that D_O has 10%–20% larger values than D_B. The decrease in the diffusivity above a certain pressure is not surprising but quite natural. It is, however, unusual that the diffusivity of O atoms is reduced more quickly than that of B atoms with compression above 10 GPa, indicating another diffusion mechanism at such high pressures. As a result, D_B becomes about two times larger than D_O when the pressure exceeds 20 GPa. Note that such pressure dependence has not been observed in the first-principles study of liquid SiO_2.[12]

To consider the anomalous diffusive properties of liquid B_2O_3 under pressure, it is worth noting that the number of fourfold-coordinated B atoms becomes larger than that of threefold-coordinated B atoms, as shown in Fig. 2(a), when D_B and D_O are interchanged. We focused on diffusion processes associated with fourfold-coordinated B atoms. A typical example is shown in Fig. 4, where the time evolution of the bond-overlap populations, $O_{ij}(t)$, associated with the B and O atoms of interest is displayed with snapshots of atomic configurations. $O_{ij}(t)$ yields a semiquantitative estimate of the strength of the covalentlike bonding between atoms.[22,23] In the beginning of this process, the B atom labeled "B1" has fourfold coordination. The atomic configuration at 0.02 ps (and also at 0.17 ps) shows that fourfold-coordinated B atoms have a tetrahedral arrangement, which demands sp^3 hybridization around them. As displayed in the top panel of Fig. 4, $O_{B1-O1}(t)$ begins to decrease at about 0.08 ps and almost vanishes for $t > 0.11$ ps. This time change means that the covalent bond between B1 and O1 is broken within 0.03 ps. On the other hand, $O_{B1-O2}(t)$ increases gradually between 0.08 and 0.15 ps, indicating that a covalent bond is formed between B1 and O2, taking 0.07 ps to form. As shown in the atomic configuration at 0.10 ps, the B1 atom has threefold coordination with a planar arrangement before the formation of the new B1-O2 bond is complete. This planar configuration is considered to be rather stable with sp^2 hybridization around the B1 atom, as seen regularly at pressures lower than 10 GPa. In this way, one of the B-O bonds is broken quickly, and a new B-O bond is formed gradually when B atoms move between the fourfold-coordinated sites.

In the diffusion process shown in Fig. 4, twofold-coordinated O atoms, toward which fourfold-coordinated B atoms move, are necessary as B1 moves toward O2. Note that O2 has twofold coordination before B1 bonds to it. As shown in Fig. 2(b), twofold-coordinated O atoms exist even at high pressures. In addition, several twofold-coordinated O atoms exist around each B atom, at least at about 50 GPa (see the bottom panel in Fig. 4). These facts indicate that this diffusion process occurs rather frequently, and that B atoms can diffuse fairly easily. On the other hand, for the concerted reaction involving the migration of O and B atoms, threefold-coordinated B and twofold-coordinated O atoms are necessary. However, the number of threefold-coordinated B atoms decreases rapidly with increasing pressure for $P > 20$ GPa, which means that the concerted reaction is suppressed at such high pressures. This is why D_O decreases rapidly with increasing pressure.

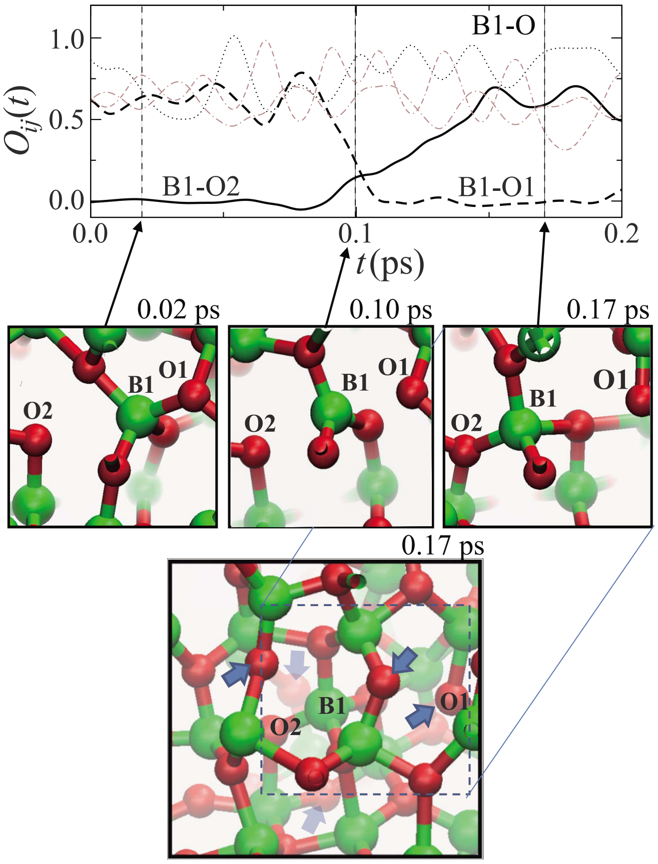

FIG. 4. (Color online) (top panel) The time evolution of bond-overlap populations $O_{ij}(t)$ for i=B1 and $j \in$ O in the diffusion process observed at 46.2 GPa. The thick solid and dashed lines show $O_{ij}(t)$ associated with the B and O atoms of interest. The thin lines show $O_{ij}(t)$ between the B atom of interest (labeled "B1") and their neighboring O atoms except O1 and O2. (middle panel) Atomic configurations at t=0.02, 0.10, and 0.17 ps. The large and small spheres show B and O atoms, respectively. (bottom panel) Extended view of the atomic configuration at t=0.17 ps. The arrows denote O atoms that are twofold-coordinated to B atoms.

It has been known that the maximum in the pressure dependence of the diffusion coefficients is absent at higher temperatures in liquid SiO_2.[12] We therefore expect that, also in liquid B_2O_3, the diffusion maximum will disappear when temperature becomes higher. However, O atoms will have lower diffusivity than B atoms with increasing pressure even at higher temperatures because B atoms will have fourfold coordination eventually, regardless of temperature. The investigation of the temperature dependence is in progress, and will be published elsewhere.

In summary, we have investigated the static and dynamic properties of liquid B_2O_3 under pressures up to about 100 GPa by *ab initio* molecular dynamics simulations. We discussed the effects of compression on the local structure based on the nearest-neighbor distances and coordination-number distribution. The pressure dependence of diffusivity has been explained successfully in terms of diffusion mechanisms.

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