**Ab initio** molecular dynamics study of diffusion mechanism in liquid B$_2$O$_3$ under pressure

Satoshi Ohmura and Fuyuki Shimojo

*Department of Physics, Kumamoto University, Kumamoto 860-8555, Japan*

E-mail: 095d9003@st.kumamoto-u.ac.jp

**Abstract.** Computer simulation based on molecular dynamics is powerful approach to clarify the microscopic mechanism of atomic diffusion in liquid state. Here, the diffusion properties and the microscopic diffusion mechanisms in liquid B$_2$O$_3$ under pressure are studied by *ab initio* molecular dynamics simulations. It is found that diffusivities of liquid B$_2$O$_3$ show anomalous pressure dependence. Diffusion coefficients of liquid materials usually decrease with pressure. However, that of liquid B$_2$O$_3$ increases with increasing pressure up to about 10 GPa. Additionally, diffusivity of boron becomes about twice larger than that of oxygen under pressure above 20 GPa. These anomalous pressure dependences are strong related to the microscopic atomic diffusion in liquid B$_2$O$_3$.

1. Introduction
In the structures of crystalline and B$_2$O$_3$ in ambient pressure, each boron atom is coordinated to three oxygen atoms, forming a triangular BO$_3$ unit, and each oxygen atom is twofold coordinated to boron atoms [1, 2]. Under compression, crystalline B$_2$O$_3$ 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 liquid state, the local coordination around each atom remains the same upon melting at atmospheric pressure [6], i.e. boron atoms are predominantly threefold coordinated to oxygen atoms, and most of oxygen atoms bridge two adjacent boron atoms. Unlike crystalline state, however, there must take place the rearrangement of the B-O covalent bonds with long-range atomic diffusion in liquid state. In terms of bond switching process of liquid B$_2$O$_3$ at ambient pressure has been investigated by first-principle molecular dynamics simulation [7]. The investigation reveals that a non-bridging 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.

The transport properties of liquid B$_2$O$_3$ under pressure have been studied by *in situ* viscosity measurements experiments [8] and *ab initio* molecular dynamics simulations [9, 10]. The former has revealed that the viscosity decreases with increasing pressure up to 8 GPa. The latter has shown that the diffusivity of atoms is enhanced by pressure below 10 GPa, as in other covalent liquids, such as SiO$_2$ and GeO$_2$ [12, 13]. Additionally, the simulation has found that the diffusivity of boron becomes about two times larger than that of oxygen under pressures.
above 20 GPa, while the former is 10–20% smaller than the latter at lower pressures. This is because the number of threefold-coordinated B atoms decreases more rapidly than that of twofold-coordinated O atoms with increasing pressure. Although it is clarified the origin of the diffusion maximum and the anomalous diffusion property under hipressure above 20 GPa, it is unclear why the diffusivity decrease with increasing pressure above 10 GPa.

In this paper, we investigate the dynamic properties of liquid B\textsubscript{2}O\textsubscript{3} under pressure by \textit{ab initio} molecular-dynamics (MD) simulations with interatomic forces calculated quantum mechanically. We focus on the diffusion mechanism under pressure including the pressure region from 10 GPa to 20 GPa in which the diffusivity decrease with pressure. The purposes of our study is to discuss the mechanism of atomic diffusion accompanied by the B-O bond exchange under pressure and to explain the pressure dependence of diffusivity in terms of microscopic diffusion mechanisms in all pressure region.

2. Method of Calculation

We use 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 [14] with a time step of \( \Delta t = 1.2 \) fs. The atomic forces were obtained from the electronic states calculated using the projector-augmented-wave (PAW) method [15, 16] within the framework of density functional theory (DFT) in which the generalized gradient approximation (GGA) [17] was used for the exchange-correlation energy. The plane-wave cutoff energies are 30 and 200 Ry for the electronic pseudo-wave functions and the pseudo-charge density, respectively. The energy functional was minimized using an iterative scheme. [18, 19] Projector functions are generated for the \( 2s \) and \( 2p \) states of B and O. The \( \Gamma \) point was used for Brillouin zone sampling. To obtain a liquid state, we began by carrying out an \textit{ab initio} MD simulation for about 5 ps at a temperature of 5000 K starting from the low-pressure crystalline phase [1]. The temperature is selected to be high enough to make the system reach a completely disordered state without the effects of the initial configuration. Then, we decreased the temperature of the system gradually to a target temperature of 2500 K. The density was taken from the extrapolation of the experimental data [20] obtained up to 1500 K. The temperature of 2500 K was chosen so as not only to be sufficiently high to maintain the liquid state even at the high pressures, but also in order to observe enough number of atomic-diffusion events to analyze the diffusion mechanism in a statistically meaningful way within a limited amount of simulation time. To determine the density of the liquid state under pressure, a constant-pressure MD simulation [21] 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 [22, 23]. The time-averaged pressure [24, 25] was calculated at each density, and we obtained the density-pressure relation as shown in Fig. 1. The thermodynamic states investigated in this study cover a density range from 1.69 to 3.99 g/cm\textsuperscript{3}, and a pressure range from 1.4 to 97.0 GPa. The quantities of interest were obtained by averaging over 14.4 \( \sim \) 21.6 ps to achieve good statistics after the initial equilibration, which takes at least 2.4 ps.

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure1.png}
\caption{Pressure dependence of the density of liquid B\textsubscript{2}O\textsubscript{3} at 2500 K}
\end{figure}
3. Result and Discussion

3.1. Pressure dependence of diffusivity

Figure 2 shows pressure dependence of diffusion coefficient and coordination number distribution obtained by our simulation. Clearly, the diffusion coefficients of B and O increase with pressure up to 10GPa. This is consistent with the experimental result that the viscosity of liquid $\text{B}_2\text{O}_3$ decrease with increasing pressure. Above 10GPa, the diffusivity decreases with increasing pressure, which 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. $D_B$ becomes about two times larger than $D_O$ when the pressure exceeds 20 GPa. Diffusion properties must be related to the weakening of the covalent interaction between atoms accompanying the increasing in the coordination number. In order 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.

2. $f^{(n)}_{\alpha-\beta}$ is the ratio of the number of $\alpha$-type atoms that are coordinated to $n$ $\beta$-type atoms to the total number of $\alpha$-type atoms. To obtain $f^{(n)}_{\alpha-\beta}$, we count the number of $\beta$-type atoms inside a sphere with radius $R$ centered at each $\alpha$-type atom, where $R = 1.9$ Å is a cutoff distance determined from the first-minimum position of $g_{\text{B-O}}(r)$ at 1.4 GPa. 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 coordination, respectively, under pressure up to about 3 GPa. 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. While $f^{(3)}_{\text{B-O}}$ and $f^{(4)}_{\text{B-O}}$ are exchanged for each other at about 25 GPa, $f^{(3)}_{\text{O-B}}$ 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.

3.2. Diffusion mechanism

In liquid $\text{B}_2\text{O}_3$, long-range atomic diffusion occurs by several diffusion mechanisms, depending on pressure. At ambient pressure, one non-bridging O atom double bonded to a twofold-coordinated B atom is always involved with atomic diffusion accompanied by the B-O bond switching. Figure 3 shows a typical example of the generation of a non-bridging oxygen, where snapshots of atomic configurations is displayed with the time evolution of the bond-overlap populations [26, 27] associated with the B and O atoms of interest. The bond-overlap populations give a semiquantitative estimate of the strength of the covalent-like bonding between atoms.

In the atomic configuration at 0.01 ps (the top panel of Fig. 3), all B and O atoms displayed are threefold- and twofold-coordinated, respectively, to hetero atoms, i.e. there is no bond defect. As shown in the bottom panel of Fig. 3, $O_{\text{B}_2-O_2}(t)$ begins to increase at about 0.04 ps, which means that a covalent bond is formed between B2 and O2 (in the snapshot at 0.07 ps). Due to
the formation of the bond, both B2 and O2 are over-coordinated. Since the over-coordination is energetically unstable, one of the covalent bonds around the threefold-coordinated O2 atom is broken (in the snapshot at 0.13 ps). Note that B1 is coordinated to only two oxygens, while B2 is still over-coordinated. Finally, the covalent bond between B2 and O1 is broken, as $O_{B2-O1}(t)$ is almost zero for $t > 0.16$ ps. While the threefold coordination of B2 is recovered, O1 is coordinated to only one boron B1 (in the snapshot at 0.19 ps). In this way, the non-bridging O atom (O1) is generated with the threefold-coordinated B atom (B1). We see that there is a double bond between B1 and O1, as $O_{B1-O1}(t)$ has higher values for $t > 0.16$ ps after the breaking of the B2-O1 bond. It should be noted that this process takes place in the participation of only two over-coordinated (one fourfold-coordinated B and one threefold-coordinated O) atoms, namely only one BO$_4$ unit.

After about 2 ps, the double bond between B1 and O1 disappears as shown in Fig. 4. First, the non-bridging O1 approaches to B3 to form a new covalent bond between them. We see that $O_{B3-O1}(t)$ gradually increases for $t > 2.01$ ps as shown in the bottom panel of Fig. 4, and that O1 is bonded to B3 in the atomic configuration at 2.08 ps. It is also seen that $O_{B1-O3}(t)$ increases for $t > 2.07$ ps, which means the formation of a covalent bond between B1 and O3 (in the snapshot at 2.11 ps). In this configuration, O1 and B1 have the proper coordination.
numbers, and instead B3 and O3 are over-coordinated. As O_{B3–O3}(t) becomes nearly zero at about 2.12 ps, the B3-O3 bond is broken, and an atomic configuration with no bond defect is finally obtained (in the snapshot at 2.18 ps).

**Figure 5.** (Top panel) Atomic configurations at $t = 0.07$, 0.16 and 0.25 ps. The large and small spheres show B and O atoms, respectively. (Bottom panel) Same as Fig. 3.

When pressure increase above 3 GPa, the usual concerted reactions with two BO$_4$ unit can take place because B atoms are more easily coordinates to four O atoms under high pressure. In Fig. 5, 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. As displayed in the snapshot at 0.09 ps, two BO$_4$ groups are generated as an intermediate by forming two new B-O bonds between adjoining BO$_3$ units, in contrast to the fact that only one BO$_4$ group is required to produce the nonbridging O atoms. The concerted reactions occur more frequently under higher pressures, which will result from the covalent-bond weakening due to the compression. Therefore, the diffusion enhancement with pressure is originated from this process. We also observed that the reactions with the nonbridging O atoms decrease with increasing pressure and almost disappear for $P > 10$ GPa.

The diffusivity of B and O atoms decrease with compression above 10 GPa. Since BO$_4$ group becomes more stable above 10 GPa, it takes longer time to exchange covalent bonds compared to the process of Fig. 5. A typical bond exchange process is shown in Fig. 6. In this process, B

**Figure 6.** (Top panel) Atomic configurations at $t = 0.05$, 0.17 and 0.43 ps. The large and small spheres show B and O atoms, respectively. (Bottom panel) Same as Fig. 3 but for B2.
atom labeled "B1" which has threefold coordination exchange O1 for O2 through BO4 group. Since BO4 group is more stable in this pressure region, B1 keeps fourfold coordination for about 0.3 ps. After that, B1 recovers to threefold coordination.

This decrease of diffusivity is quite natural in liquid materials. It is, however, unusual that the diffusivity of O atoms is reduced more quickly than that of B atoms. In order to consider this anomalous pressure dependence of diffusion coefficient, it is worth noting that the number of fourfold-coordinated B atoms is much larger than that of threefold-coordinated B atoms while both twofold- and threefold-coordinated O atoms exist as shown in Fig. 2. We focused on diffusion processes associated with fourfold-coordinated B atoms shown in Fig. 7. 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 sp3 hybridization around them. As displayed in the bottom panel of Fig. 7, 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. The B1 atom has threefold coordination with a planar arrangement before the formation of the new B1-O2 bond is complete (in the atomic configuration at 0.10 ps). 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.

![Figure 7. (Top 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) Same as Fig. 6.](image_url)

In the diffusion process shown in Fig. 7, 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. This fact indicates 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 process is origin of rapid decreasing of D_O with increasing pressure.

4. Summary
We have investigated the diffusion properties and the microscopic diffusion mechanisms in liquid B_2O_3 under pressure by ab initio molecular dynamics simulation. It is found that long-range atomic diffusion in liquid B_2O_3 occurs by several diffusion mechanisms, depending on pressure.
Anomalous pressure dependence of diffusivity has been explained successfully in terms of these diffusion mechanisms.

Acknowledgments
The present work was supported by KAKENHI (Grant-in-Aid for Scientific Research (B) No. 23340106 and Grant-in-Aid for JSPS Fellows No. 22-1853). The authors acknowledge support by Hamamatsu Photonics K.K., Japan. They furthermore thank the Research Institute for Information Technology, Kyushu University for the use of its facilities. The computations were also performed using the computer facilities at the Supercomputer Center, Institute for Solid State Physics, University of Tokyo.

References
[1] Gurr G E, Montgomery P W, Knutson C D and Gorres B T 1970 Act. Cryst. B26 906.
[2] Johnson P A V, Wright A C, and Sinclair R N 1982 J. Non-Cryst. Solids 50 281.
[3] Prewitt C T and Shannon R D 1968 Act. Cryst. B24, 869.
[4] Nieto-Sanz D, Loubeyre P, Crichton W, and Mezouar M 2004 Phys. Rev. B 70, 214108.
[5] Lee S K, Eng P J, Mao H, Meng Y, Newville M, Hu M Y, and Shu J 2005 Nature Mater. 4, 851.
[6] Sakowski J and Herms G 2001 J. Non-Cryst. Solids 293-295, 304.
[7] Ohmura S and Shimojo F, 2008 Phys. Rev. B 78, 224206.
[8] Brazhkin V V, Farnan I, Funakoshi K, Kanzaki M, Katayama Y, Lyapin A G, and Saitoh H, 2010 Phys. Rev. Lett. 105, 115701.
[9] Ohmura S and Shimojo F, 2009 Phys. Rev. B 80, 020202(R).
[10] Ohmura S and Shimojo F, 2010 Phys. Rev. B 81, 014208.
[11] Dieffenbacher J and McMillan P F 2001 J. Phys. Chem. A 105, 7973.
[12] Karki B B, Bhattarai D, and Stixrude L 2007 Phys. Rev. B 76, 104205.
[13] Hoang V V, Zung H, and Hai T N 2007 J. Phys.: Condens. Matter 19, 116104.
[14] Tuckerman M, Berne B J and Martyna G J 1992 J. Chem. Phys. 97, 1990.
[15] Blöchl P E 1994 Phys. Rev. B 50, 17953.
[16] Kresse G and Joubert D 1999 Phys. Rev. B 59, 1758.
[17] Perdew J P, Burke K and Ernzerhof M 1996 Phys. Rev. Lett. 77, 3865.
[18] Kresse G and Hafner J 1994 Phys. Rev. B 49, 14251.
[19] Shimojo F, Kalia R K, Nakano A and Vashishta P 2001 Comp. Phys. Comm. 140, 303.
[20] Macedo P B, Capps W, and Litovitz T A 1966 J. Chem. Phys. 44, 3357.
[21] Martyna G J, Tobias D J, and Klein M L 1994 J. Chem. Phys. 101, 4177.
[22] Nosé S 1984 Mol. Phys. 52, 255.
[23] Hoover W G 1985 Phys. Rev. A 31, 1695.
[24] Nielsen O H and Martin R M 1985 Phys. Rev. B 32, 3780.
[25] Corso A D and Resta R 1994 Phys. Rev. B 50, 4327.
[26] Mulliken R S 1955 J. Chem. Phys. 23, 1841.
[27] Shimojo F, Nakano A, Kalia R K, and Vashishta P 2008 Phys. Rev. E 77, 066103.