Structure and Correlation Between the Fraction of Structural Units and Bond Angle Distribution in Liquid B$_2$O$_3$ Under Compression

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Abstract
Structure of network-forming liquid B$_2$O$_3$ is investigated by Molecular dynamics simulation (MDS) at 2000K and in the 0-40 GPa pressure range (corresponding to the 1.71-3.04 g/cm$^3$ density range). Results indicate that network structure of liquid B$_2$O$_3$ comprises of basic structural units BO$_y$ and BO$_3$. The topology and size of BO$_y$ and BO$_3$ units at different densities are identical. The O-B-O and B-O-B partial bond angle distributions (BADs) can be determined through the fraction of BO$_3$ and BO$_2$ units. Furthermore, the total BADs are directly related to the partial BADs and the fraction of structural units. It means the fraction of units BO$_y$ ($y = 3, 4$) and units OB$_y$ ($y = 2, 3$) can be determined from the experimental BADs. The spatial distribution of BO$_3$ and BO$_2$ units is not uniform but forming clusters of BO$_3$ and BO$_2$. This leads to the polymorphism in liquid B$_2$O$_3$. It also shows that the dynamical heterogeneity in liquid B$_2$O$_3$ due to the lifetimes of BO$_3$ and BO$_2$ units are very different. The structural heterogeneity is origin of spatially heterogeneous dynamics in liquids B$_2$O$_3$.

Keywords: Boric oxide B$_2$O$_3$, Molecular Dynamics Simulation, Network Structure, Polyamorphism, Heterogeneous Dynamics.

Introduction
Boric oxide (B$_2$O$_3$) is one of the simplest glass-forming oxides and it is also one of the most important materials with many high-technology applications. Due to its important applications in optical materials and glass ceramics, borate glasses and melts have been investigated by both experiment and computer simulation. The experimental results of Lee, et al. indicate a change coordination number of B-O pair from 3 to 3.46 as pressure increases from 4.1 to 7.3 GPa and increase up to 3.92 at 22.5 GPa [1]. Structural study of B$_2$O$_3$ glass by X-ray diffraction was carried out by Warren and he showed that network structure of B$_2$O$_3$ consists of BO$_3$ units which link to each other via bridging oxygen [2]. The boron atoms in the structure of pure B$_2$O$_3$ glass are mostly related to BO$_3$ ring. The B$_2$O$_3$ rings will be broken and BO$_y$ and BO$_3$ units are formed when Na atoms (modifier atoms) are added [3]. Further, modifier atoms also change the dynamical and physical properties along with structural modifications. Investigation by X-ray diffraction in indicated that the O-B-O, O-O-O and B-O-B BADs in B$_2$O$_3$ glass have a main peak located at about 120$^\circ$, 60$^\circ$ and 120$^\circ$, respectively [4]. There is small sharp peak at 60$^\circ$ in the B-B-B BAD. This results in the presence of many planar boroxol rings (B$_2$O$_4$). However, the fraction of boron atoms in the B$_2$O$_4$ boroxol rings still in debate [5-9]. According to neutron diffraction experiment, Philip S Salmon showed that at ambient pressure, the mean bond distance and the mean coordination number of B-O atomistic pair is corresponding to about 1.35 Å and around 3.0. The studies showed that, the structures of crystalline B$_2$O$_3$ is built by BO$_3$ units (at low pressure) and BO$_2$ units (at high pressure) [10-16]. The transformation from BO$_3$ units to BO$_2$ units happens at 6.5 GPa. For B$_2$O$_3$ liquid, the local structure unchanged as temperature increase up to melting point (at ambient pressure) [17]. The MDS found that non-bridging oxygen linked to a twofold-coordinated boron [18]. This defect coordination relates to atomic diffusion and results in rearrangement of the covalent bonds. Satoshi Ohmura indicated anomalous diffusion in liquid B$_2$O$_3$ by ab initio MDS [19]. Diffusion coefficients of B and O atoms in liquid B$_2$O$_3$ increases as pressure increases to 10 GPa. Although B$_2$O$_3$ has been investigated for many decades but so far, its structure is still debate and requires more studies. One among interesting directions of recent studies is to clarify network structure, relation between structure and dynamic properties. These issues are very difficult to conduct by experiment and ones usually apply the simulation method. MDS can track trajectories of each atom over whole simulation time. Thus, by using MDS, we can get insight into the network structure and dynamics properties of liquid B$_2$O$_3$ under high pressure. MDS in recent works concerning B$_2$O$_3$ reveal that a gradual transition from BO$_3$ unit to BO$_2$ unit induces the variation of total O–B–O and B–O–B BADs [16-22]. It means that there is a correlation between the total O–B–O, B–O–B BADs and the fraction of structural units. However, as far as we know, the correlation between the total O–B–O, B–O–B BADs and the fraction of structural units in liquid B$_2$O$_3$ is not clarified. Besides, the number of studies on the polymorphism and dynamical heterogeneity in liquid B$_2$O$_3$ is very limited. In this work, the structural characteristics, polyamorphism and dynamical heterogeneity in liquid B$_2$O$_3$ will clarified. Especially, the correlation between the fraction of structural...
units and BADs in liquid $B_2O_3$ will be discussed in detail.

**Calculation method**

MDS is carried out for $B_2O_3$ system containing 3000 atoms at temperatures of 2000 K and in the 0-40 GPa pressure range by using Born-Mayer-Huggins potential. The detail of this potential can be found in Ref. [23]. The MD initial configuration is built by randomly placing 3000 atoms in a simulation box with periodic boundary conditions. This sample is equilibrated at temperature of 6000 K to remove the effect of remembering initial configuration after 2.106 MD steps. Then, the sample is cooled down to the temperature of 2000 K and at ambient pressure. The model M1 will be obtained after being relaxed for a long time in an NPT ensemble (number of atom N, pressure P and temperature T are constant). From model M1, by compressing to different pressures (different densities) and then relaxed for a long time to reach the equilibrium, we will obtain 8 models at different densities from 1.71 to 3.04 g/cm$^3$. To improve the statistics the measured characteristics such as the coordination number, partial radial distribution function (PRDF) are computed by averaging over 1000 configurations separated by 10 MD steps. To evaluate the coordination number and BAD, we use the cut-off distance is 1.90 Å. Here, the cut-off distance is chosen as the position of the first minimum of PRDF $g_{ij}(r)$. To obtain the dynamics characteristics, the computational models were also relaxed for a long time in the NVE ensemble (number of atom N, Volume V and Energy E are constant). The spatial distribution of units $BO_3$ and $BO_4$ is also clarified via visualization technique.

**Result and Discussion**

**Pair radial distribution functions**

The density dependence of the PRDF $g_{ij}(r)$ is showed figure 1. In $g_{BO}(r)$, the first peak position locates at about 1.36 Å over all densities and becomes more asymmetric with increasing density. After the first peak, there is a very broad peak appears around 2.96 Å in the model when the density approaches 2.96 g/cm$^3$. This peak is related to the appearance of ring structure at higher density (figure 2). The $g_{BO}(r)$ and $g_{BB}(r)$ is strongly dependent on density. For $g_{BO}(r)$, the first peak shift to left and the height of peak decreases as density increases. For $g_{BB}(r)$, the location of first peak is unchanged but the height of peak decreases as density increases. The $g_{BO}(r)$ and $g_{BB}(r)$ relates to intermediate-range order (IRO). It means that the IRO structure of liquid $B_2O_3$ is strongly dependent on density. Detail about of structural characteristics of $B_2O_3$ is shown in table 1. The simulation results for liquid $B_2O_3$ show a good agreement with experimental data as well as simulation of other works in peak position [4,10,19].

![Figure 1: Pair radial distribution functions of liquid $B_2O_3$ at different densities](image)

![Figure 2: Ring structure in $B_2O_3$](image)

**Table 1: Structural characteristics of liquid $B_2O_3$, $r_{ij}$ - position of first peak of PRDF $g_{ij}(r)$; $Z_{ij}$- the mean coordination number; $Bx, Oy$ - the fraction of structural unit $BOx$ and linkage $OB_x$.**

<table>
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<th>Models</th>
<th>M1</th>
<th>M2</th>
<th>M3</th>
<th>M4</th>
<th>M5</th>
<th>M6</th>
<th>M7</th>
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$^{a,b,c}$Experiment and simulation data in [10], [4], [19] respectively.

**Distribution of B-O and O-B coordination number**

Figure 3 shows the density dependence of fraction of coordination units $BxO$ ($x=3,4$) and $OBy$ ($y=2,3$). The results show that at low density (1.71 g/cm$^3$) the B-O coordination number distribution is characterized by frequencies 3 (98%), 2 (2%) with mean coordination number $ZBO=3.02$. The coordination number distribution O-B is characterized by frequencies 2 (99%), 3 (1%) with mean coordination number $ZO-B=2.01$. It means that at low density, structure of $B_2O_3$ is built up by units $BO_3$ and forms continuous random network of the units. The $BO_3$ basic structural units link each to other via $OB_3$ linkages at low density. With increasing density, the fraction of units $BO_4$ monotonously decreases, while the fraction of units $BO_3$ monotonously increases. At high density (3.04 g cm$^{-3}$), the network structure of liquid $B_2O_3$ comprises of both $BO_3$ and $BO_4$ units linked each to other via $OB_3$ or $OB_4$ linkages. The B-O coordination number distribution is characterized by frequencies 4 (67%), 3 (33%) with mean coordination number $ZBO=3.69$. The coordination number distribution O-B is characterized by frequencies 2 (56%), 3 (44%) with mean coordination number $ZOB=2.46$. We can see that there...
is a gradual transition from units \( \text{BO}_3 \) to \( \text{BO}_4 \) with increasing the density. Note that a transition starts to appear when the density approach 2.80 g/cm\(^3\). The units \( \text{BOx} \) is connected to each other through common oxygen atoms forming random network structure in three-dimensional space, (figure 4). The simulation results about coordination number as well as bond length, bond angle is also showed a good agreement with experiment and simulation results [4,10,19].

Figure 3: Distribution of B-O and O-B coordination number as a function of density

Figure 4: The continuous random network of \( \text{BO}_3 \) units in three-dimensional space at 2.44 g/cm\(^3\), the \( \text{BO}_3 \) forming region with black color, the \( \text{BO}_4 \) forming region with red color.

The bond angle and the bond length distributions

To clarify the topology and network structure, the O-B-O and B-O-B bond angle distribution are investigated in detail. The O-B-O bond angle relates to topology of units \( \text{BOx} \) and B-O-B bond angle relates to the connectivity between the \( \text{BOx} \) units (network structure). Figure 5 shows partial O-B-O BADs for units \( \text{BOx} \) (x=3, 4). The results show that the partial O-B-O BAD in \( \text{BO}_3 \) or \( \text{BO}_4 \) units is almost the same for different models (different densities). This means that the O-B-O BADs in \( \text{BO}_3 \) or \( \text{BO}_4 \) units do not depend on density. The partial B-O-B BADs for coordination units \( \text{OBy} \) (y=2, 3) is showed in figure 6. The BAD in \( \text{OB}_2 \) linkages depends strongly on density meanwhile the BAD in \( \text{OB}_3 \) linkages does not depend on density. The partial B-O BAD in coordination units \( \text{BO}_3 \), \( \text{BO}_4 \) is shown in figure 7. For all kinds of coordination units \( \text{BOx} \), the B-O bond length decreases with increasing density. The above analysis demonstrates that the bond angle and bond length distribution in \( \text{BOx} \) units is not dependent of pressure. In other word, the topology structure of \( \text{BOx} \) units in different models is identical. With increasing density, liquid \( \text{B}_2\text{O}_3 \) gradually transforms from the network structure of \( \text{BO}_3 \) (at low density) to network structure of \( \text{BO}_4 \) (at high density). These results are good agreement with experimental data [4].

Figure 5: The O-B-O bond angle distribution in \( \text{BO}_3 \) and \( \text{BO}_4 \) units

Figure 6: The B-O-B bond angle distribution in \( \text{OB}_2 \) and \( \text{OB}_3 \) linkages

Figure 7: The B-O bond distance distribution in \( \text{BO}_3 \) and \( \text{BO}_4 \) units
The correlation between the fraction of structural units and bond angle

We will focus on investigating BADs and establishing the correlation between the fraction of structural units and total BADs. To establish the correlation, let \( n_y \) denote the number of units \( \text{BO}_y \) (\( x = 3, 4 \)). The total number of O-B-O angles in \( \text{BO}_x \) and \( \text{BO}_y \) is \( 3nB3, 6nB4 \), respectively. We denote \( m_{n}(\theta) \) to the number of angles in interval \( \theta \pm d\theta \) in units \( \text{BO}_x \). The probability that given angle in interval \( q \) \( \pm d\theta \) in a sample is given by

\[
g_B(\theta) = \frac{m_{n}(\theta)+m_{3n}(\theta)}{3n_{B3}+6n_{B4}} = 3A\frac{g_{B3}(\theta)}{g_{B3}(\theta)+6A\frac{g_{B4}(\theta)}{g_{B4}(\theta)}}B_3 + 6A\frac{g_{B4}(\theta)}{g_{B4}(\theta)}B_4.
\]

Here \( A = (n_y + n_2)/(3n_y + 6n_2) \); \( g_{B3}(\theta) = m_{B3}(\theta)/3n_{B3} \); \( g_{B4}(\theta) = m_{B4}(\theta)/6n_{B4} \). The function \( g_B(\theta) \) in fact represents the probability that the given O-B-O angle in units \( \text{BO}_x \) lies in the interval of \( \theta \pm d\theta \). Therefore, the function \( g_B(\theta) \) described the total O-B-O BAD can be expressed via the fraction \( B_x \) and functions \( g_B(\theta) \) which represent the partial BAD for units \( \text{BO}_x \). Here notation \( B_x \) (\( x = 3, 4 \)) is the fraction of \( \text{BO}_x \) in sample. The value of \( B_x \) is given in table 1. Because the topology structure of \( \text{BO}_x \) units in different models is identical so there are the common functions \( g_B(\theta) \) for all considered models. These functions are presented in Figure 6. For both kind of units \( \text{BO}_x \) and \( \text{BO}_y \), function \( g_B(\theta) \) has a form of Gauss function and a pronounced peak at 115°; the case of \( \text{BO}_x \) function \( g_B(\theta) \) has a peak at 115°. Figure 8 shows the total O-B-O BADs for \( \text{BO}_3 \) models together with the result calculated by equation (1) at different densities. The total O-B-O BAD changes strongly with density. Its main peak slightly shifts to lower angle and the height at different densities. The total O-B-O BAD changes strongly with density. Its main peak slightly shifts to lower angle and the height decreases strongly, while the lifetime of \( \text{BO}_4 \) phases and \( \text{BO}_3 \)-phase are expanded and \( \text{BO}_4 \)-phase are shrunk. At 3.04 g/cm\(^3\), the regions with \( \text{BO}_4 \)-phase are nearly expanded whole model. The clusters of \( \text{BO}_4 \)-phase form low density regions, conversely clusters of \( \text{BO}_3 \) form high density regions. The size of low- and high-density regions is strongly dependent on density (pressure). It means that there is a structural phase transformation from \( \text{BO}_3 \)-structural phase to \( \text{BO}_4 \)-structural phase with increasing density. Furthermore, in the Figure 11, the lifetime of \( \text{BO}_3 \) decreases strongly, while the lifetime of \( \text{BO}_4 \) increases. Result shows that at low density, the structure of liquids \( \text{BO}_4 \), mainly consist of \( \text{BO}_3 \) phases and lifetime of units \( \text{BO}_4 \) is very long in comparison with the one of units \( \text{BO}_3 \). In contrast, at high density, the structure of above liquid mainly consists of \( \text{BO}_4 \)-phases and the lifetime of time of units \( \text{BO}_4 \) is shorter the one of units \( \text{BO}_3 \). This means that \( \text{BO}_3 \)-phase will form mobile regions while \( \text{BO}_4 \)-phases will form immobile regions. This leads to the polyamorphism or structural heterogeneity in 5 liquid \( \text{BO}_x \). Furthermore, the structural heterogeneity in liquids \( \text{BO}_x \) is origin of spatially heterogeneous dynamics.

### Structural and dynamical heterogeneities

To clarify the structural and dynamical heterogeneities in liquids \( \text{BO}_x \), we have visualized the spatial distribution of \( \text{BO}_x \) and calculated the mean lifetime of the structural units \( \text{BO}_x \). Figure 10 showed that the distribution of coordination units \( \text{BO}_x \) is not uniform, but they tend to form the cluster of units \( \text{BO}_x \). It means that in the considered density range the structure of liquid \( \text{BO}_x \) comprises two structural phases: \( \text{BO}_x \)-structural phase (black color), \( \text{BO}_x \)-structural phase (red color). From figure 9 at low density (1.90 g/cm\(^3\)) the regions with units \( \text{BO}_4 \) are linked to each other forming a large region (\( \text{BO}_4 \)-phase) expanding nearly whole model. The regions with units \( \text{BO}_4 \)-phase are very small and localized at different locations. With increasing density, the regions with \( \text{BO}_4 \)-phase are expanded and the regions with \( \text{BO}_3 \)-phase are shrunk. At 3.04 g/cm\(^3\), the regions with \( \text{BO}_4 \)-phase are nearly expanded whole model. The clusters of \( \text{BO}_3 \) form low density regions, conversely clusters of \( \text{BO}_4 \) form high density regions. The size of low- and high-density regions is strongly dependent on density (pressure). It means that there is a structural phase transformation from \( \text{BO}_3 \)-structural phase to \( \text{BO}_4 \)-structural phase with increasing density. Furthermore, in the Figure 11, the lifetime of \( \text{BO}_3 \) decreases strongly, while the lifetime of \( \text{BO}_4 \) increases. Result shows that at low density, the structure of liquids \( \text{BO}_4 \), mainly consist of \( \text{BO}_3 \) phases and lifetime of units \( \text{BO}_4 \) is very long in comparison with the one of units \( \text{BO}_3 \). In contrast, at high density, the structure of above liquid mainly consists of \( \text{BO}_3 \)-phases and the lifetime of time of units \( \text{BO}_4 \) is shorter the one of units \( \text{BO}_3 \). This means that \( \text{BO}_3 \)-phase will form mobile regions while \( \text{BO}_4 \)-phases will form immobile regions. This leads to the polyamorphism or structural heterogeneity in 5 liquid \( \text{BO}_x \). Furthermore, the structural heterogeneity in liquids \( \text{BO}_x \) is origin of spatially heterogeneous dynamics.
Conclusion
In this work, MDS methods were applied for investigating the structure and correlation between the fraction of structural units and bond angle distribution of liquid B$_2$O$_3$ under compression. Results show that the structure of B$_2$O$_3$ comprises basic structural units BO$_x$ ($x=3, 4$) and OB$_y$ ($y=2, 3$) linkages. At low density, most of basic structural units are BO$_3$. At high density, most of basic structural units are BO$_4$. Under compression, there is a transformation from BO$_3$-network structure (at low density) to BO$_4$-network structure (at high density) in network structure of liquid.

The partial bond angle and bond length distribution in BO$_x$ units is not dependent on density. The topology structure of units BO$_x$ and OB$_y$ linkages at different densities is identical. As a result, all models have the same partial BADs $g_{BO}(\theta)$ and $g_{OB}(\theta)$. This result allows us to establish a simple correlation between the BADs and the fractions of BO$_x$ units and OB$_y$ linkages. The simulation results show a good agreement with data calculated by obtained expression for both total B-O-B and O-B-O BADs. The distribution of units BO$_x$ is not uniform, but it tends to form clusters of BO$_3$, BO$_4$. With increasing density, the size of regions with BO$_1$-phase decreases and the size of regions with BO$_2$-phase increases. The BO$_3$-phase forms mobile regions, while BO$_4$-phase forms immobile regions. Polyamorphism or structural heterogeneity in liquids B$_2$O$_3$ is the structural origin of spatially heterogeneous dynamics.

Acknowledgement
This work was supported by Hanoi University of Science and Technology - T2017-PC-139.

References