

Polyamorphism and Structural Transformation in Liquid B_2O_3 under Compression: Insight from Visualization of Molecular Dynamics Data

Mai Thi Lan*, Nguyen Thu Nhan, Nguyen Van Hong

*Department of Computational Physics, Hanoi University of Science and Technology
No. 1 Dai Co Viet, Hanoi, Vietnam*

Received 13 February 2014

Revised 14 March 2014; Accepted 28 March 2014

Abstract: The structural order, polyamorphism and structural change of liquid B_2O_3 at 3000 K and in a 0-40 GPa pressure range are investigated by molecular dynamics simulation. Results show that the network structure of liquid B_2O_3 is formed from BO_x basic structural units ($x=3, 4$). At ambient pressure, most of basic structural units (coordination units) are BO_3 (over 99%). The BO_3 basic structural units are linked each to other via OB_2 linkages. At high pressure, the network structure of liquid B_2O_3 comprises of both BO_3 and BO_4 units linked each to other via OB_2 or OB_3 linkages. The bond angle and bond length distribution in BO_x units is not dependent of pressure. In other word, the topology structure of BO_x units in different models is identical. The bond angle distribution in OB_2 linkages depends strongly on pressure meanwhile the bond angle distribution in OB_3 linkages does not depend on pressure. With increasing pressure, liquid B_2O_3 transforms gradually from a BO_3 - network structure (at low pressure) to BO_4 - network structure (at high pressure). The distribution of BO_x in model is not uniform but tends to form the clusters of BO_x units. The clusters of BO_3 the form low density regions, conversely the clusters of BO_4 form the high density regions. The size of low and high density regions is strongly dependent of pressure.

Keywords: Polyamorphism, molecular dynamics simulation, B_2O_3 , structure.

1. Introduction

Local structure, polyamorphism and polymorphic transformations in network forming liquid under high pressure and temperature are very interesting and widely studied topics of physics and material science. Liquid B_2O_3 and SiO_2 are typical network-forming liquids with many similar properties (forming continuous random network structure; exhibiting anomalous diffusion behaviour, polyamorphism and polyamorphic transformations under compression). At ambient pressure, the structural order in short range of both liquid and glass B_2O_3 is characteristic by BO_3 basic structural

* Corresponding author. Tel.: 84-988277387
Email: lan.maithi@hust.edu.vn

units. The basic structural units are linked each to other through bridging oxygen atom forming continuous random network in three-dimensional space. Under compression, the structure of liquid and glass transforms from low- to high-density (liquid) amorphous phases characterized by a coordination increase from three to four (the short range order transforms from BO_3 to BO_4 units) and by significant variations in the IRO. This is evidence of polyamorphism in B_2O_3 . Specially, nuclear magnetic resonance experiment in recent work [1-5] shown that the fraction of BO_3 units involved in boroxol rings (B_3O_6) in glass B_2O_3 decreases gradually with increasing pressure. At pressure below 5 GPa, most of basic structural units is BO_3 (BO_4 units are absent in glasses at pressure below 4 GPa). However, the findings are in contrast with the results of a previous NMR study on hot densified glassy B_2O_3 which shown that: the fraction of BO_3 units increasing from about 0.75 at ambient pressure to about 0.8 at 2 GPa, then substantially decreasing to about 0.41 at 6 GPa; it is also existence of BO_4 units at pressure below 2 GPa and the fraction of BO_4 unit increasing as pressure of synthesis increases.

2. Calculation

Molecular dynamic (MD) simulation is carried out for B_2O_3 systems (2000 atoms) at temperatures of 3000 K and pressure range from 0 to 40 GPa. The ‘‘Buckingham Potential’’ potential is used and detail of them can be found in Ref. [1]. Initial configuration is obtained by randomly placing all atoms in a simulation box. This sample is equilibrated at temperature of 7000 K and then cooled down to the temperature of 3000K. A consequent long relaxation has been done in the NPT ensemble (constant temperature and pressure) to obtain a sample at ambient pressure which is denoted to model M1. The models at different pressures were constructed by compressing model M1 to different pressures and then relaxed for a long time to reach the equilibrium. In order to improve the statistics the measured quantities such as the coordination number, partial radial distribution function are computed by averaging over 1000 configurations separated by 10 MD steps.

3. Result and discussion

3.1. Coordination units

Figure 1 shows the pressure dependence of fraction of coordination units BO_x ($x = 3, 4$) and OB_y ($y=2,3$). At ambient pressure, most of basic structural units (coordination units) are BO_3 (over 99%). With increasing pressure, the fraction of units BO_3 monotonously decreases, while the fraction of units BO_4 monotonously increases. The pressure dependence of fraction of units OB_y is similar to the one of units BO_x . It can be seen that, most of basic structural units are BO_3 and the BO_3 basic structural units are linked each to other via OB_2 linkages at ambient pressure. At high pressure, the network structure of liquid B_2O_3 comprises of both BO_3 and BO_4 units linked each to other via OB_2 or OB_3 linkages. The units BO_x are connected to each other through common oxygen atoms forming random network structure in three-dimensional space, see figure 2.

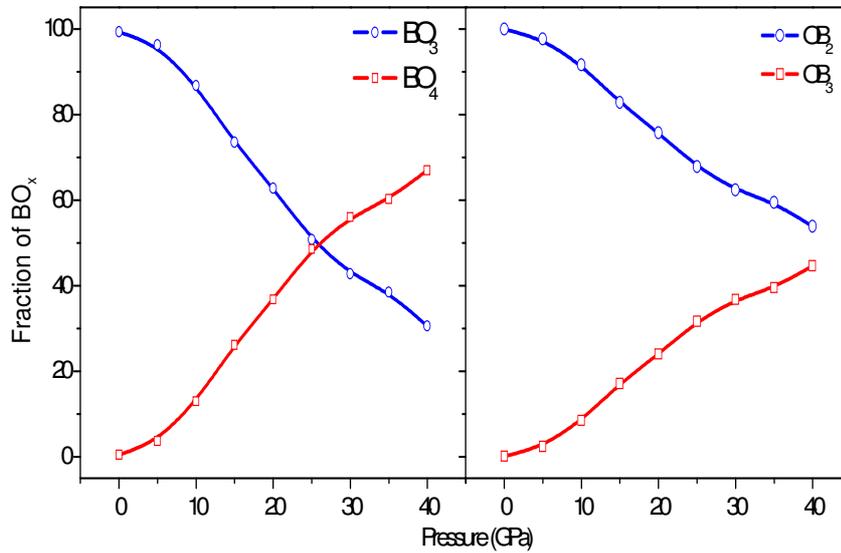


Fig.1. Distribution of coordination units BO_x ($x = 3, 4$) and OB_y ($y=2,3$) as a function of pressure.

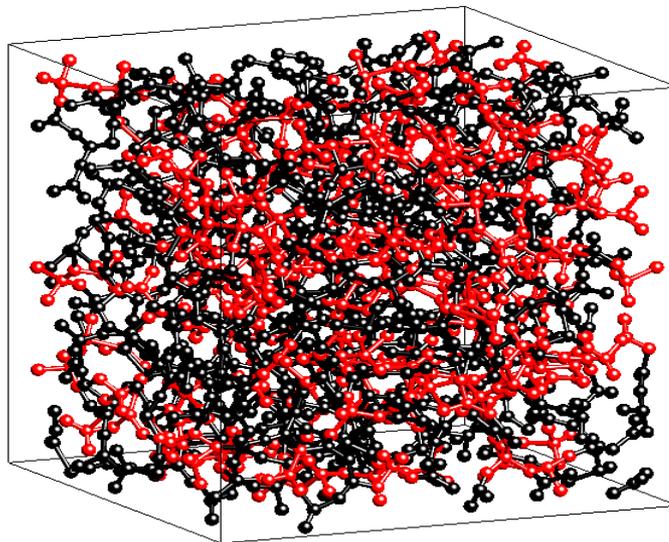


Fig.2. The continuous random network of BO_x units in three dimension space at 15 GPa, the BO_3 forming region with black color, The BO_4 forming region with red color.

3.2. The bond angle and the bond length distribution

Figure 3 shows partial O-B-O bond angle distributions for coordination units BO_x and the bond angle between two adjacent coordination units BO_x ($x=3,4$). The results show that the partial O-B-O bond angle distribution in each kind of coordination unit is almost the same for different models (different pressures/ densities). This means that the O-B-O bond angle distributions in coordination units BO_x do not depend on pressure. The partial B-O-B bond angle distributions for coordination units OB_y and the bond angle between two adjacent coordination units OB_y ($y=2,3$) is showed in figure 4. The bond angle distribution in OB_2 linkages depends strongly on pressure meanwhile the bond angle distribution in OB_3 linkages does not depend on pressure. The partial B-O bond length distribution in coordination units BO_3 , BO_4 is shown in figure 5. It can be seen that for all kinds of coordination units BO_x , the B-O bond length decreases with increasing pressure. The above analysis demonstrates that the bond angle and bond length distribution in BO_x units is not dependent of pressure. In other word, the topology structure of BO_x units in different models is identical. With increasing pressure, liquid B_2O_3 transforms gradually from a BO_3 - network structure (at low pressure) to BO_4 - network structure (at high pressure).

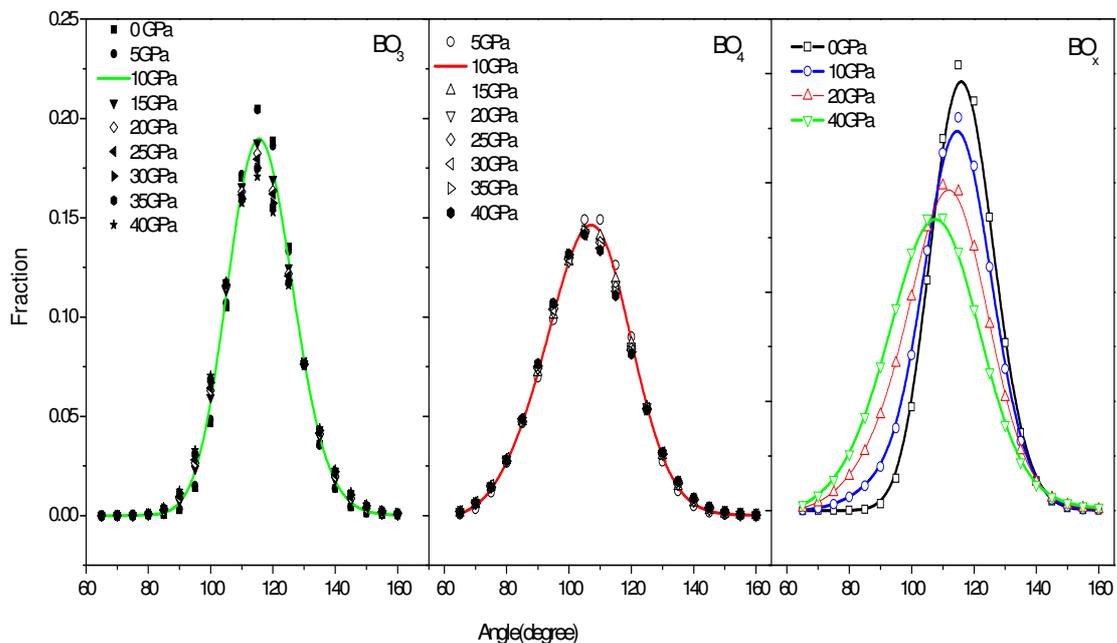


Fig. 3. The bond angle distribution in coordination units BO_x ($x=3,4$) and the bond angle between two adjacent coordination units BO_x .

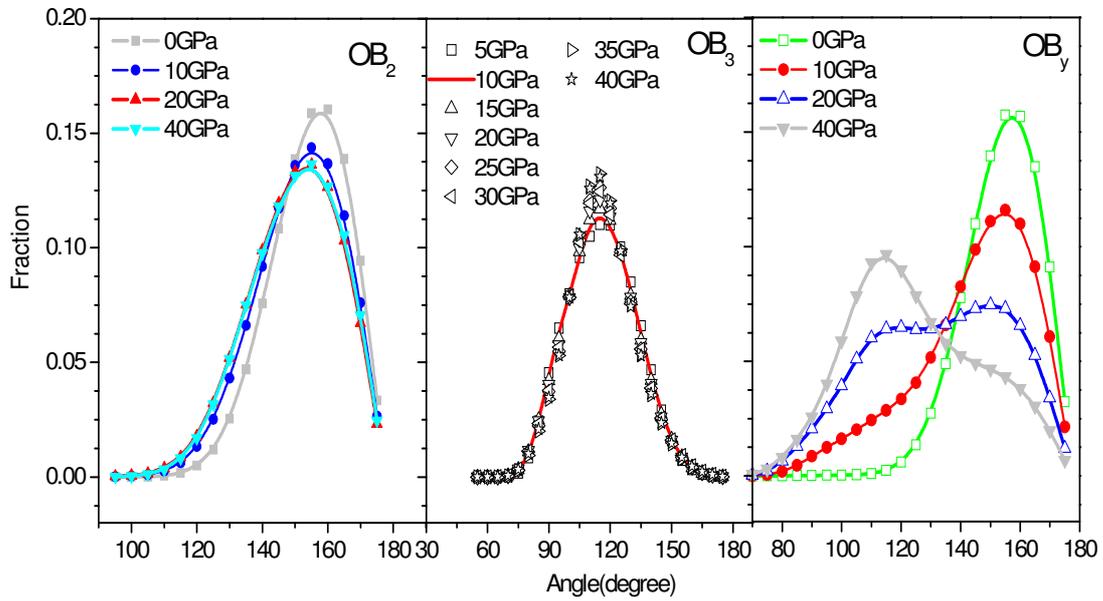


Fig. 4. The bond angle distribution in coordination units OB_y ($y=2,3$) and the bond angle between two adjacent coordination units OB_y .

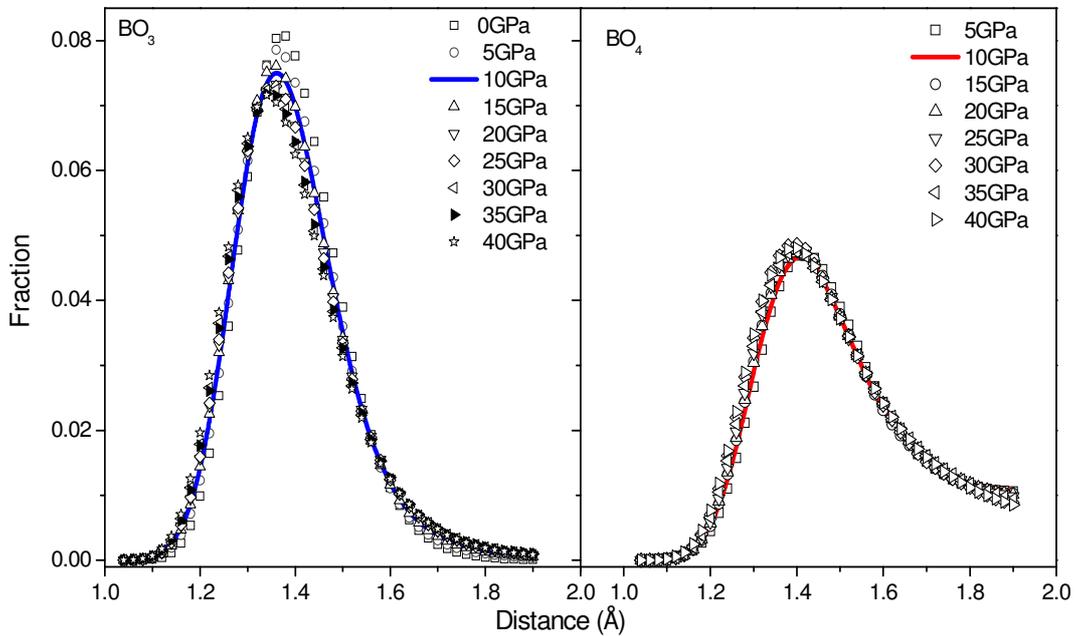


Fig. 5. The bond length distribution in coordination units BO_x ($x=3,4$).

3. The network structure and polyamorphism

To clarify the network structure and polyamorphism, we have visualized the distribution of BO_x in B_2O_3 system at different pressures (see Figures 6, 7 and 8). Figures 6 and 7 show the spatial distribution of BO_3 , BO_4 and mixture of BO_x at different pressures. It can be seen that the distribution of coordination units BO_x is not uniform but they trend to form the cluster of units BO_x . From figure 8, it can be seen that the distribution of units BO_x is not uniform but forming the cluster of BO_3 , BO_4 . It means that in the considered pressure range the structure of liquid BO_x comprises two structural phases: BO_3 -structural phase (black color), BO_4 -structural phase (red color). From figure 8, it can be seen that, at low pressure (5 GPa) the regions with BO_3 -phase are linked each to other forming a large region expanding nearly whole model. The regions with BO_4 -phase are very small and localized at different locations. With increasing pressure, the regions with BO_4 -phase are expanded and the regions with BO_3 -phase are shrunk. At 40 GPa, the regions with BO_4 -phase are nearly expanded whole model. The clusters of BO_3 form low density regions, conversely clusters of BO_4 form high density regions. The size of low and high density regions is strongly dependent of pressure. It means that there is a structural phase transformation from BO_3 -structural phase to BO_4 -structure with increasing pressure.

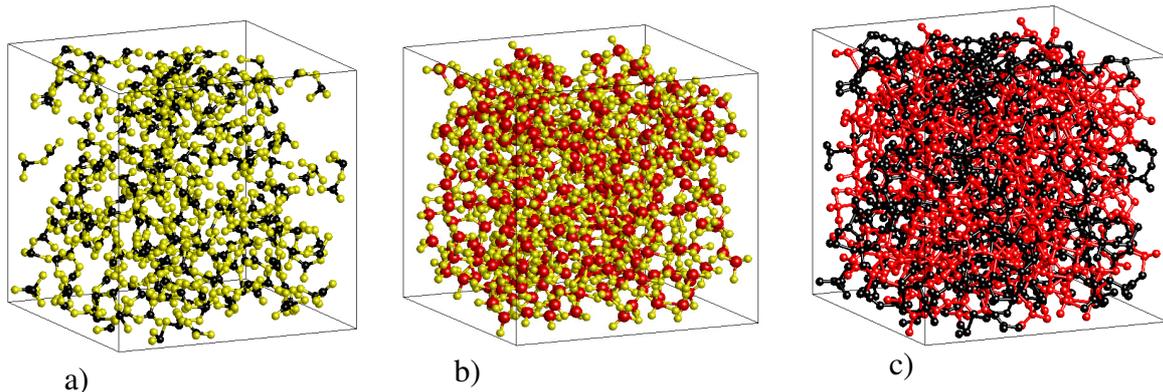


Fig.6 . Spatial distribution of units BO_3 (a), units BO_4 (b), and mixture of units BO_3 and BO_4 in B_2O_3 (c). Model is constructed at 40 GPa.

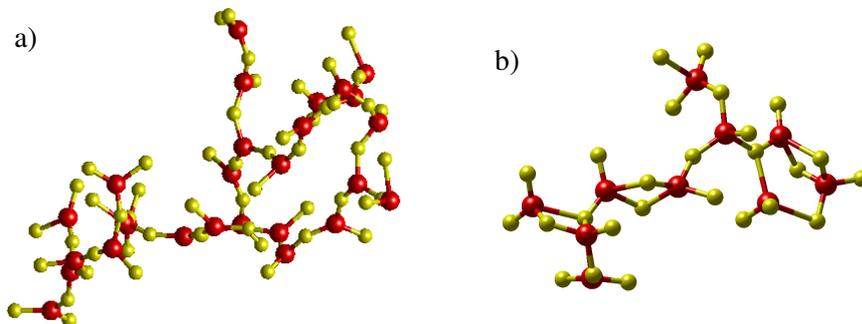


Fig.7. Cluster of BO_3 (a) and BO_4 units (b).

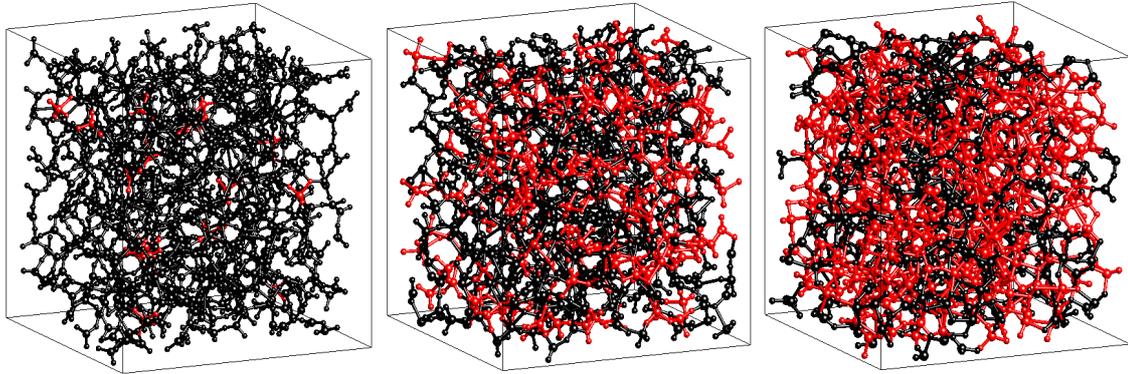


Fig.8 . Spatial distribution of basic structural units BO_3 , BO_4 in B_2O_3 at 5 GPa (a); 15 GPa (b); 40 GPa (c). Region with black color is BO_3 -structural phase; red color is BO_4 -structural phase.

4. Conclusion

Polyamorphism and structural transformations in liquid B_2O_3 under compression have been studied by mean of the molecular dynamic simulation. Results show that the structure of B_2O_3 comprises basic structural units BO_x ($x=3,4$). The bond angle and bond length distribution in BO_x units is not dependent of pressure. The topology of units BO_x at different pressures is identical. The distribution of units BO_x is not uniform but it trends to form clusters of BO_3 , BO_4 . With increasing pressure, the size of regions with BO_3 -phase decreases and the size of regions with BO_4 -phase increases. The liquid B_2O_3 transforms gradually from a BO_3 - network structure (at low pressure) to BO_4 - network structure (at high pressure).

Acknowledgments

This research is funded by Vietnam National Foundation for Science and Technology Development (NAFOSTED) under grant number 103.05-2013.30.

References

- [1] E. Kashchieva, B. Shivachev, Y. Dimitriev, "Molecular dynamics studies of vitreous boron oxide", *Journal of Non-Crystalline Solids* 351 (2005) 1158–1161.
- [2] L.D. Pye, V.D. Frechette, N.J. Kreidl (Eds.), *Proc. Conf. on Borate Glasses Structure, Properties, Applications*, Plenum, New York, 1977.
- [3] A.C. Wright, S.A. Feller (Eds.), *Proc. Sec. Int. Conf. on Borate Glasses, Crystals and Melts*, Society of Glass Technology, Sheffield, 1997.
- [4] S.A. Feller, in: Y.B. Dimitriev, A.C. Wright (Eds.), *Proc. Third. Int. Conf. on Borate Glasses, Crystals and Melts*, Society of Glass Technology, Sheffield, 2001, p. 1.
- [5] Y.B. Dimitriev, A.C. Wright, in: M. Affatigato, St. A. Feller, N.M. Vedishcheva, A.C. Wright (Eds.), *Proc. Fourth Int. Conf. on Borate Glasses, Crystals and Melts*, Society of Glass Technology, Sheffield, 2004, p. xix.