MATERIALS SCIENCE : STRUCTURE

Nature of Structural Transformations in the B_2O_3 Glass under High Pressure

Atomic rearrangements and phase transformations in glasses under high pressure (polyamorphism) are one of the most intriguing and puzzling topics of physics.

B_2O_3 represents an archetypical oxide glass alongside such glasses as SiO_2 and GeO_2, with the important difference that at the ambient conditions, the structural units are planar BO_3 triangles as opposed to tetrahedra. The *in situ* investigations of B_2O_3 glass under pressure have been performed previously by using Raman and Brillouin spectroscopies [1], and through inelastic X-ray scattering spectroscopy [2]. Besides, there have been attempts to examine the B_2O_3 glass under pressure by molecular dynamics computer simulation, using empirical inter-atomic potentials [3,4]. According to the data of [1] B_2O_3 glass under compression experiences a transformation in the pressure range P~ 6-15 GPa, with the reverse transformation at decompression occurring sharply at P~ 3 GPa. According to the Ref. [2] B_2O_3 glass, under compression, features a considerable change in the bonding type in the 6-20 GPa pressure range. It should be underlined that the quantitative estimates of the degree of transformation based on the indirect experiments [2] and those based on the computer simulation data with empirical potentials [3,4] are drastically different.

In [5] we report the results of the *in situ* diffraction experiments, *in situ* volumetric measurements, and complement them with the data from *ab initio* calculations. The *in situ* structural study of the B_2O_3 glass has been done at the beamline **BL14B1**. The *in situ* volumetric measurements of the B_2O_3 glass were conducted by the strain gauge technique. We have used the SIESTA method for high-pressure *ab initio* simulations.

The *in situ* diffraction structural data for the B_2O_3 glass at different pressures are presented in Fig. 1. At P < 5 - 6 GPa, the 1st peak of the total correlation function does not change. The basic changes take place in the distant coordination spheres. At higher pressures the structural changes begin affecting the 1st coordination sphere: the fraction of the 4-coordination boron atoms can be assessed as being about 40-45% at P~ 9.5 GPa, T~ 650 K.

Glass structures under compression from *ab initio* simulations are shown in Fig. 2. At high pressures glass structure consists mostly of BO_4 tetrahedra (Fig. 2 (b,c)). At the initial stage of the coordination transformation (P ~ 5-7 GPa) there is a slight shift of the B-O average distance whereas the fraction of

the 4-coordinated boron is close to zero. One can suppose that it is associated with the distortion of BO_3 triangles. The *ab initio* simulations indeed show that before transforming into the 4-fold coordination, BO_3 triangles loose their planarity, as the B atom is pushed out of the plane of three O atoms starting from 4 - 5 GPa.
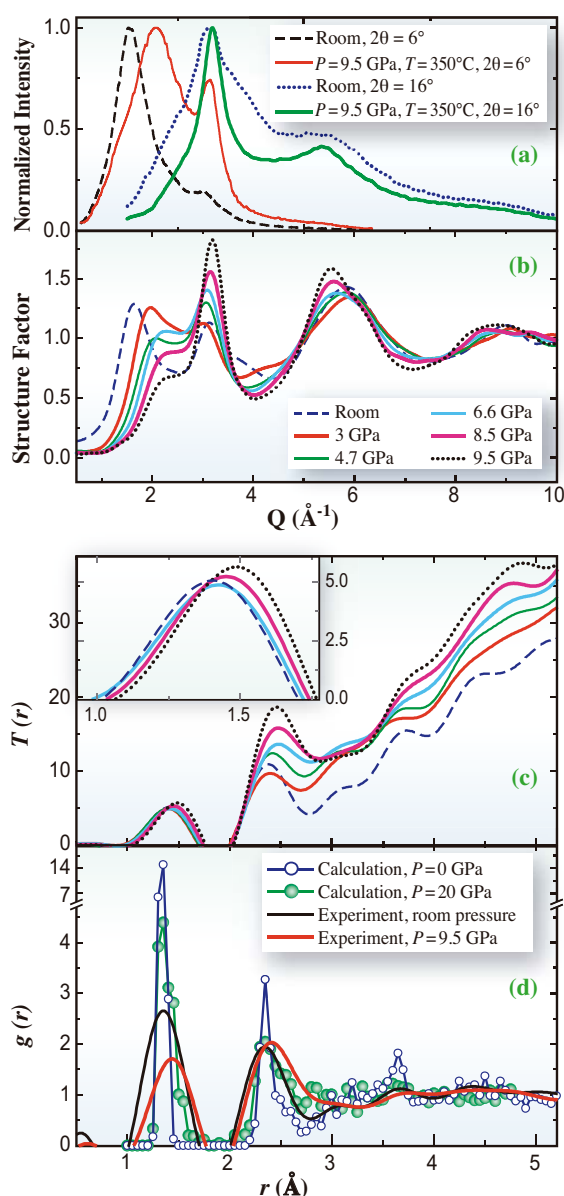

Fig. 1. Examples of the energy dispersive X-ray diffraction (EDXD) data for the glassy B_2O_3 **(a)**, measured at different pressures at the two angles of the detector; calculated from the experimental EDXD data structure factor **(b)**; total correlation function **(c)**, and comparison of the experimental and computer simulated structural correlation functions for different pressures **(d)**. All experimental curves for $P = 9.5$ GPa correspond to the sample obtained after heating to 650 K.

The "relaxed" bulk modulus of the B_2O_3 glass obtained from the volumetric measurements does not increase monotonically: the transformation in the B_2O_3 glass consists of two broad overlapping transitions occurring at P > 1 GPa and P > 5 GPa. The 1st transformation corresponds to the structural changes in the distant coordination spheres, while the 2nd one at P > 5 GPa conforms to the coordination transformation in glass. The coordination transition is fully reversible. The decrease of the coordination of the boron atoms from 4 to 3 begins at P~4.5 GPa and ends at P~1 GPa. This transformation is smooth in hydrostatic conditions. Therefore, the conclusion made in Ref. [1] about the first-order character of this transition is untrue and is likely to be an artifact associated with strongly non-hydrostatic conditions near the sample.

Figure 3 presents the comparison of the experimental and calculated coordination changes with pressure. A reasonable agreement between experiment and first-principles calculations can be seen. As follows from this figure, previous simulations with empirical potentials significantly underestimated the fraction of increased coordination, especially the results from [4], whereas previous inelastic X-ray scattering data [2] overestimated the coordination changes under compression.

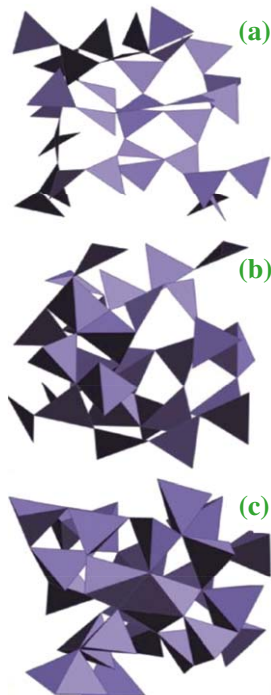The first-principles simulations enable us to analyze the behavior of glass at much larger pressures than those available in the experiments that use large volume presses. We observe that unlike its crystalline counterpart BO_4 tetrahedra in glass at high pressure can be connected in edges (see Fig. 1(b)). The fraction of edge-shared tetrahedra increases with density, and under further compression face-shared tetrahedra with 5- and 6-coordinated B atoms appear in the glass (Fig. 1(c)).

The present study demonstrates the necessity of direct structural measurements and direct volumetric measurements and importance of *ab initio* computer simulation study. The interpretation of indirect study of structural transformation, e.g. using inelastic X-ray scattering data, should be considered with caution.
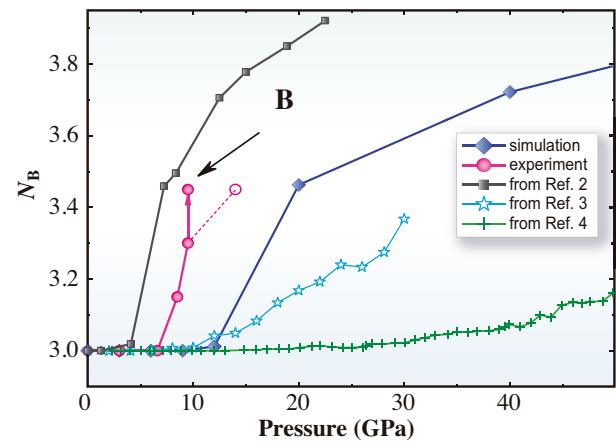

Fig. 3. Pressure dependences of the 1st coordination number for B from the current experiment (X-ray diffraction) and simulation and according to the data from Refs. [2-4]. Point B in the experimental dependence corresponds to the heated sample, whereas the open point is the estimation of the point B position which should be observed under room-temperature compression.

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Fig. 2. Polyhedron representation of the simulated B_2O_3 glass structure at zero pressure (a), P = 20 GPa (b), and P = 200 GPa (c), where triangles correspond to the BO_3 structure units (3-fold coordinated boron), tetrahedrons - to BO_4, and there are the single BO_5 and BO_6 units on (c).

References

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