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In-situ observation of the structural change in MgO-B_2O_3-SiO_2 glass at high pressure and the permanent structural change

A. Yamada[a,b,*], M. Harada[b], A. Masuno[c,d,e,f], K. Yamanaka[g], Y. Higo[h], S. Yoshida[a,b], T. Ohta[g], J. Matsuoka[a,b]

[a] Center for Glass Science and Technology, The University of Shiga Prefecture, 2500, Hassaka-cho, Hikone, Shiga 522-8533, Japan
[b] Department of Material Science, The University of Shiga Prefecture, 2500 Hassaka-cho, Hikone, Shiga 522-8533, Japan
[c] Graduate School of Science and Technology, Hirosaki University, 3 Bunkyo-cho, Hirosaki, Aomori 036-8561, Japan
[d] Institute of Industrial Science, The University of Tokyo, 4-6-1 Komaba Meguro-ku, Tokyo 153-8505, Japan
[e] Laboratory for Materials and Structures, Tokyo Institute of Technology, 259 Nagatuta-cho, Midori-ku, Yokohama, Kanagawa 226-8503, Japan
[f] Center for Materials Research by Information Integration, Research and Services Division of Materials Data and Integrated System, National Institute for Materials Science, 1-2-1 Sengen, Tsukuba, Ibaraki 305-0047, Japan
[g] SR Center, Ritsumeikan University, 1-1-1 Nojihigashi, Kusatsu, Shiga 525-8577, Japan
[h] Japan Synchrotron Research Institute, SPring-8, 1-1-1, Sayo-cho, Koto, Hyogo 679-5148, Japan

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ABSTRACT

A 41.6MgO-27.1B_2O_3-31.2SiO_2 glass was synthesized by container-less levitation method. B *K*-edge X-ray absorption near edge structure (XANES) spectroscopy was used to quantify the coordination of boron in the as-made glass, resulting in ~72% of boron in 3-fold coordination. Raman spectroscopy indicated that the glass structure includes depolymerized borate units, which are pyroborate ($B_2O_5^{4-}$) and ring and/or chain-type metaborate ($B_3O_6^{3-}$, $(BO_2O^-)_\infty$) groups. The structural changes in the glass under hydrostatic condition were investigated by high-pressure Raman spectroscopy within a diamond anvil cell at pressures up to 8.5 GPa. On the borate structure, metaborate groups decreased with pressure. In contrast, triborate groups, which include tetrahedrally coordinated boron and have a fully polymerized borate network, increased; suggesting that the coordination transformation of B and polymerization were induced via compression. However, the modification of the borate structure units seems to be reversible at least up to 8.5 GPa. As for the silicate network, Q^0 and Q^1 structures were responsible to compression. Specifically, Q^0 could be replaced by Q^1 with elevating pressure, which means that the silicate network becomes polymerized with pressure. Whereas, structure of glass samples recovered from the pressure higher than 5 GPa displayed depolymerized silicate network, as dissociation of Q^2 to Q^1. The observed structural changes in the silicate network implied a partial change of the coordination number of Si^{4+} ions, which can be enhanced by the presence of a modifier cation with high field strength such as Mg^{2+}.

1. Introcudtion

It is widely known that glass materials are "brittle". Thus, development of hard and tough glasses has been a long withstanding challenge. In a previous study, the addition of MgO to the glass composition made the resulting glass tougher [1,2]. In specific, the Crack Resistance, *CR*, which is defined with load where two cracks initiate in the indentation test using Vickers indenter, was fairly improved in the Mg-bearing silicate glass. The addition of Mg makes glass harder due to the high single bond strength and field strength ($=Z/r_i^2$ where Z and r are charge and the ion radius of the i ion, respectively), which make the structure depolymerized and closed packed. However, in many cases, the hardness and toughness of the material are in a trade-off relationship. It was proposed from diffraction studies that MgO polyhedra, which are widely regarded as a "network modifier", could form a periodic network in highly MgO-containing glass (Mg_2SiO_4 glass: [3]). Additionally, previous studies on Mg bearing glasses have highlighted the possibility of polyhedral linkage of MgO_x units in the glass structure (e.g., [4,5]). Consequently, MgO polyhedra in the glass may play a role of "network former" like SiO_2, B_2O_3 and so on. Such a construction of network in glass structure should improve the toughness of glass material.

Various structural modifications can happen when the material is subjected to stress. Some of the strengthened materials take advantage

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* Corresponding author at: Center for Glass Science and Technology, The University of Shiga Prefecture, 2500, Hassaka-cho, Hikone, Shiga 522-8533, Japan.
E-mail address: yamada.ak@mat.usp.ac.jp (A. Yamada).

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of stress-induced structural change (e.g., tensile stress: tetragonal to monoclinic transformation in stabilized ZrO_2). The modification of the glass structure under stress condition could, therefore, have an influence on the mechanical strength. However, in many cases, the structural changes under pressurized condition are reversible unless the stress exceeds the threshold (i.e., permanent densification, e.g., silica glass: [6]). Hence, in-situ observation on the structure in glass material under stressed condition is necessary for accurate understanding the structural evolution with elevating stress.

In this study, a relatively high MgO-bearing borosilicate glass was synthesized by container-less method. The structure of as-made glass was investigated by B *K*-edge X-ray absorption near edge structure (XANES) and Raman spectroscopy. Additionally, the elastic properties were measured using the pulse-echo overlapping method. Furthermore, the structural response of the glass to hydrostatic compression was examined by high-pressure Raman spectroscopy using a diamond anvil cell, up to ~8.5 GPa.

2. Experimental setup

2.1. Sample preparation

Although the glass-forming ability in $MgO\text{-}B_2O_3\text{-}SiO_2$ system has been poorly investigated, sample composition, $40MgO\text{-}30B_2O_3\text{-}30SiO_2$ (molar percent), was chosen based on the previous study on the phase relationship [7] and the report in which glass synthesis has been successfully done [8]. Furthermore, since the composition includes relatively high amount of MgO, it is suitable to investigate the effect and the role of MgO.

The starting oxide mixture was prepared from MgO (Kanto Chemical Co. Inc.), B_2O_3 (Kishida Chemical Co. Ltd.) and SiO_2 (Sigma Aldrich). The B_2O_3 powder was put in high-temperature desiccator (80 °C) for ~20 h then cooled down to room temperature to minimize the effect of water before weighting. In order to enhance reaction and avoid compositional heterogeneousness in the glass, SiO_2 was grinded solely to < ~5 μm grain size before mixing with other oxides. The three oxides were mixed with appropriate ratio (total weight was ~30 g) and grinded for ~1 h. Then, the starting powder was compressed to obtain the pellet with the shape of column (ϕ ~7.7 mm). Finally, The starting sample for the container-less method was obtained by sintering the pellets at ~950 °C for ~20 h.

Homogeneous glasses were obtained in the previous work [8] by repeating conventional melting procedure (melted at 1350 °C). However, in this study, small amount of crystallization could not be avoided with the melting method, probably due to the insufficient quenching rate and/or heterogeneous nucleation from crucible. Thus, container-less method (e.g., [9]) by gas-flow laser-heating apparatus has been exploited for the glass synthesis in this study. The heating was performed by irradiation of CO_2 laser from both sides of sample to minimize the thermal gradient. Simultaneously, the sample (~20 mg) was levitated with O_2 gas flow, which was well controlled during the heating to keep the sample gravitationally neutral. The heating of the sample was monitored directly with a CCD camera. Once the sample was melted, the laser was cutted off for quenching the sample. Finally, transparent, colorless and spherical glass samples (~2-mm diameter) were obtained. Usually, the experiment was finished quickly, within a couple of minutes, to prevent evaporation loss from the sample. The glass sample was obtained with a 87% yield in weight, which corresponds to ~13% loss of B_2O_3 in weight assuming that solely B_2O_3 was evaporated in heating process. Thus, the composition of the obtained glass can be estimated as $41.6MgO\text{-}27.1B_2O_3\text{–}31.2SiO_2$ (molar percent).

2.2. Measurement of physical properties

The densimetry of the sample was conducted with sink-float method, because the mass of the as-made glass was quite small, ~20 mg. Firstly, the density standard was prepared by mixing 1,1,2,2-tetrabromoethan and 1,1,2,2-tetrachloroethan to be approximately close to the density as the glass sample. Then, the relationship between temperature and density of the mixture was calibrated with pycnometer to be density standard. Finally, the glass sample was put in glass cylinder with the density standard, then the temperature was slowly decreased from 50 to 45 °C while observing the position of the glass sample in the glass cylinder. The density of glass sample can be determined when the glass begins to float assuming that the density of the liquid and glass is completely equal. In the present method, density is obtainable with the accuracy within ± 0.001 g/cm^3.

The spherical glass samples were polished on both sides with 1-μm Al_2O_3 compound. The elastic wave velocities were measured by the pulse-echo overlapping method, which is suitable for the measurement of thin samples [10]. A $LiNbO_3$ (10° Y cut) crystal, which can generate transverse and longitudinal waves simultaneously, was used for the transducer. Frequency was set to 60–120 MHz for a sample length of 1.0–1.5 mm. The travel times were determined in order to analyze the reflected echoes from surface to backside of sample. The sampling interval of the digital oscilloscope used in this measurement was 100 ps. The ultrasonic wave velocities can be derived dividing the sample length by the travel time as following equation.

$$V_{L,T} = l/2t_{L,T}$$

where $V_{L,\,T}$, l and $t_{L,\,T}$ are ultrasonic wave velocity, sample length and travel time for longitudinal and transversal waves, respectively. Further, Young's modulus, shear modulus, bulk modulus and Poisson's ratio can be derived with below equations.

$$\text{Young's modulus} = 2\rho V_T^2[1 + (V_L^2 - 2V_T^2)/2(V_L^2 - V_T^2)]$$

$$\text{Shear modulus} = \rho V_T^2$$

$$\text{Bulk modulus} = \rho(V_L^2 - 4/3V_T^2)$$

$$\text{Poisson's ratio} = (V_L^2 - 2V_T^2)/2(V_L^2 - V_T^2)$$

where ρ is the density measured by the method described above. The uncertainty for the moduli in this study is 0.8%.

2.3. Structural analysis

In order to quantify the proportion of boron coordination, B *K*-edge XANES spectroscopy was performed at BL-2, where soft X-ray is available, using synchrotron X-ray radiation from AURORA in SR center, Ritsumeikan University. The white X-ray from storage ring was monochromated with the grating (180–230 eV). Then the X-ray was slitted to the size of 0.1 × ~20 mm (vertical × horizontal) by downstream slits to irradiate to the sample. The measurement was conducted using the fluorescence yield method, in which photoelectrons are detected with micro-channel plate placed in a back scattering geometry. The relationship between photon energy and channel of detector was calibrated with the white line of boron nitride (192.0 eV). The proportion of boron coordination in this study has an uncertainty of 0.7%. This uncertainty was estimated from the standard deviation of ten (10) measurements on the same sample.

Raman spectroscopy (NRS-5100, JASCO) was also applied to identify the borate and/or silicate superstructure in the glass, which consists of the linkage of the fundamental structural units such as tetrahedrally coordinated Si and/or B (SiO_4, $^{[4]}B$) and triangularly coordinated B ($^{[3]}B$). The probe light (532-nm excitation wavelength) was irradiated to the sample, and then the scattered light was detected with CCD detector placed at 180-degree (backward).

2.4. High-pressure Raman spectroscopy

In this study, a Diamond anvil cell (e.g., [11]) was employed for the