Structural investigation of Mg and B polyhedra in high Mg-baring borosilicate glasses

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The demand to an improvement in the strength of glass is increasing further. In the previous research, the toughness of glass increases by replacing a part of glass composition by MgO [1]. MgO in glass materials seems to influence the strength of glass. Therefore, it becomes useful knowledge towards the further improvement in the strength of glass material to clarify the structural role. Mg in glass structure has been considered to be *modifier ion* that divides the borosilicate network structure. However, recent studies have revealed that Mg in high Mg content silicate glass partially have a four-coordinated structure and form a network structure [2]. However, it is difficult for the oxide glass which consists of multicomponent system with a complicated structure to analyze the structural information about a specific element. Especially the structural information on Mg in glass structure is difficult to be analyzed due to its technical limitations. In this study, we aim to obtain information on the local structure of Mg and B in MgO-B_2O_3-SiO_2 system glass using X-ray absorption fine structure (XAFS) analysis with high element selectivity, with few restrictions on sample amount.

The glass composition investigated in this study is 5 compositions in MgO-B_2O_3-SiO_2 system. These glasses were synthesized by the container-less method using a gas floating laser heating apparatus. We prepared the semi-sintered sample which processed the oxide powder of the target compositions at 900 to 1000°C beforehand. They were broken into pieces of ~ 200 mg and placed at the tip of the nozzle from which oxygen gas spouted. The sample was heated and melted by adjusting the flow rate of oxygen gas, suspending the semi-sintered body, irradiating a CO_2 laser, and gradually increasing the output. The melting of the sample was confirmed by the image with a CCD camera, and vitrification was performed by quenching the melted sample, cutting the laser power. The sample shapes were all collected in spherical shape (diameter ~ 2 mm) due to the influence of gas floating. The obtained glasses were polished, and XAFS measurements were performed on the polished surface.

Mg and B K-edge EXAFS measurements were performed at Ritsumeikan University SR Center BL-13 and BL-11, respectively. The measurement mode was the fluorescence yield mode which detects a fluorescent X-ray with a silicon drift detector. Raman spectroscopy was performed with a backscattering geometry using an excitation wavelength of 532 nm.

For the radial structure function obtained by Mg K-edge EXAFS measurement, the Mg−O interatomic distance in each glass was 2.04−2.01 Å, and no clear composition dependency was observed. When the Mg coordination number was estimated from the EXAFS analysis, it was suggested that MgO with a five-coordination structure exists as the main component.

In the B K-edge XANES spectra, π* peak derived from three-coordinated boron, which is observed at ~194 eV in the three spectra, appears stronger than the broad peak group at the post edge. This result suggests that a large amount of three-coordinated boron is present in the glasses. The peak deconvolution of the spectrum was performed according to the previous research [3] to determine the fraction of boron coordination. The prepared glasses exhibited 80% or more of a three-coordinated structure of boron. Furthermore, as a result of Raman spectroscopy measurement, it was found that particularly in the case of a high MgO content glass, a large amount of three-coordinated boron monomer (BO_3^{3-}) is present. It implies that a dense, highly ionic glasses are formed by the interaction between Mg^{2+} of high *field strength* and the structures having low degree of polymerization.

References

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