The structure and mechanical properties of highly MgO-bearing borosilicate glass

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Glass toughness is increased by replacing part of the glass composition with MgO[1]. For the improvement of the strength in glasses, MgO has a great influence not only on its effect but also on the network forming component such as SiO_2, B_2O_3 and so on. However, there are not many researches investigating the origin of the strength of such a glass from the viewpoint of the structure. Boron in the glass structure changes the coordination number from three to four coordinates with the substitution amount of the network modifier. It is known that when the amount of substitution is further increased, it changes again to a three-coordinate structure. The structural change of such a network-forming component influences various physical properties of the glass so that quantitative analysis is indispensable for understanding the physical properties. Therefore, in this study, we aim to analyze the boron coordination number in MgO-B_2O_3-SiO_2 glasses by XANES and clarify the glass structure using XANES and the Raman spectroscopy.

The glass compositions investigated in this study are $40MgO$-$30B_2O_3$-$30SiO_2$, $40MgO$-$20B_2O_3$-$40SiO_2$ and $60MgO$-$20B_2O_3$-$20SiO_2$ (hereafter referred to as 433, 424 and 622 glasses, respectively). These glasses were synthesized by a containerless method using a gas floating laser heating device. B K-edge X-ray absorption measurement was performed at BL-11 in SR Center, Ritsumeikan University. The spectra were measured in a fluorescence yield method with a silicon drift detector.

The observed B K-edge XANES greatly differs depending on the change of MgO / B_2O_3, in which the first peak position near 193-195 eV characteristically changes. The 433 and 622 glasses show spectra very similar to the crystals consisting only of the three-coordinated boron ($B^{[3]}$) reported in the previous work[2]. To quantify the coordination number of boron, the integrated intensity ratio of the first peak of the spectrum obtained and the broad peak seen near 200 eV was determined according to the previous study[2]. The ratio of $B^{[3]}$ in 433, 424, 622 glasses was estimated to be 82, 48, and 66%, respectively. It is found that the ratio of the four-coordinated boron ($B^{[4]}$) has a maximum of 424 glasses. In the MgO-B_2O_3 system, it has been reported that the ratio of $B^{[4]}$ has a maximum of MgO: B_2O_3 = 1: 1[3].

As a result of the Raman spectroscopy, a remarkable peak is observed in the 622 glass at a higher wave number side than around 1200 cm^{-1}. These are peaks attributed to the structure of the de-polymerized borate composed of B^3, suggesting that the 622 glass has a structure de-polymerized than other glasses and has a dense structure. The Young's modulus of the 622 glass is 136 GPa, which is a considerably high value as the glass material.

Based on the ratio of $B^{[3]}$, $B^{[4]}$ estimated by XANES, the average dissociation energy of each glass was calculated, and the 622 glass showed the highest value. The extremely high modulus of elasticity of the 622 glass is achieved by both of the “closed” structure and the strength of the bond. On the other hand, the crack resistance, which is an index indicating "difficulty in cracking", is higher for 424 glass. From the results of the XANES measurement, it is known that 424 glass contains a relatively large amount of $B^{[4]}$. The four-coordinated boron has no non-bridging oxygen and forms a complicated network structure in the glass. The network structure works favorably against resistance to "cracking".

References

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