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Investigation on the orientation of boron in anisotropic borosilicate glass

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High temperature treatment of glasses at high pressure induces structural changes. Structures of glass depend on heat treatment conditions such as thermal history and load stress because glasses are categorized as non-equilibrium materials. Generally, pristine glass is an isotropic material. However, the previous study has reported that orientation of the chain structure of glass network is orientated by tensile stress at high temperature (1).

Boron in borosilicate glasses exists as 3- or 4-coordinated state, and the fraction depends on the content of alkaline and alkaline earth metal element so-called "*modifier element*". The 3-coordinated boron forms trigonal planar and shows high structural anisotropy. Thus, we expected that the orientation of 3-coordinated boron caused by differential stress could induce an anisotropy of borosilicate glasses. Actually, two glasses, $20Na_2O$-$35B_2O_3$-$45SiO_2$ (NBS) and $49CaO$-$28B_2O_3$-$23SiO_2$(CBS) (mol%), exhibited the anisotropy by applying differential stress under high temperature and high pressure. In addition, the optical axis is perpendicular to the compression axis, which implied the orientation of the structure. However, the structural information on the structural origin of the anisotropy has not been known well yet. In this study, B K-edge X-ray absorption near edge structure (XANES) measurements were performed to reveal the relation between the anisotropy and the orientation of 3-cooditnated boron.

Differential stress was applied to NBS and CBS glasses at 4 GPa and several temperatures for 1 h. The recovered glasses were polished along with the two directions, which are parallel to the compression axis (vertical direction) and perpendicular to the compression axis (horizontal direction), respectively. Anisotropy and the direction were confirmed by retardation measurements using a polarizing microscope equipped with Babinet compensator, and the magnitude of the anisotropy was quantified by birefringence, which can be calculated from normalization of the retardation value with sample thickness. B K-edge XANES measurements were carried out in BL-11 at the SR center (Ritsumeikan University). The samples were set, as the horizontal plane is perpendicular to the X-ray optical axis. X-ray irradiation angle, θ, was varied with rotating the angle of the sample folder. Thus, contribution of the vertical plane in the spectra increases with θ.

Fig.1(a) shows the spectra of NBS with θ. The intensity of spectra was normalized by π^* peak at 193 eV, which has been assigned to 3-coordinated boron. The intensity of σ^* peak at 198 eV seems to be changed comparing to that of π^* peak with changing θ. Fig. 1(b) and (c) show the relation between θ and the peak intensity ratio defined as π^*/σ^*. The π^*/σ^* was dramatically changed as θ in NBS heated at 300°C, which exhibited the largest birefringence in the synthesized NBS samples. Such the change was also confirmed in CBS samples where π^*/σ^* was mostly changed as θ in the sample heated at 400°C showing the largest birefringence in those samples. These results manifest that the intensity of the π^*/σ^* and the θ dependence has a correlation to the birefringence and the direction. The present observation is consistent with the previous study on h-BN consists of 3-coordinated boron with preferred orientation (2). Consequently, correlation of π^*/σ^* and θ observed in this study suggests that the 3-coordinated boron could contribute to the anisotropy in borosilicate glass.

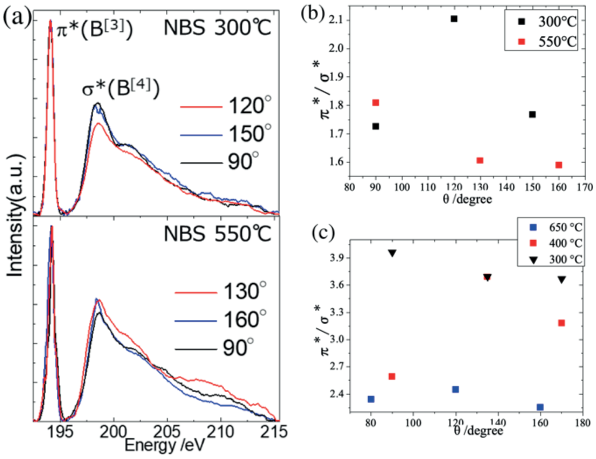

Fig. 1 B K-edge XANES spectra of NBS at treated at 300 and 550°C (a), the incident angle dependence of peak height ratio π^*/σ^* in NBS(b), that in CBS(c).

References

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