Change in boron coordination number in sodium borosilicate glass with thermal history

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1. Introduction

Boron in glass exists in 3- or 4-coordinated state depending on alkaline content in glass and/or on temperature. In particular, Non-Bridging Oxygen (*NBO*), which has an influence on various physicochemical properties of glass, is thought to be bonded to the triangularly coordinated boron. Therefore, to understand the relationship between boron coordination and the thermal history could contribute to control of glass properties, optimization of processing condition, and further, invention of new glass material. In this study, X-ray Absorption Near Edge Structure (XANES), which could be promising and powerful tool for the element-selective analysis, is applied to characterization of the glass structure. In this note, from the results of B K-edge XANES spectroscopy with ultra-soft x-ray, the coordination number of boron in alkaline borosilicate glasses is determined, and effect of thermal history is discussed.

2. Experimental

The oxide mixture with the composition of $25Na_2O$-$25B_2O_3$-$50SiO_2$ (mol%) was melted in a platinum crucible at 1200°C and held for an hour. Then, the melt was poured on the iron plate to be "original" glass. The glass obtained was annealed at 10°C higher than its glass transition temperature (T_g) for an hour to release residual stress. The glasses were heat treated at 550°C (near T_g of original glass), 450°C or 650°C. After the heat treatment, the glasses were quenched into water to prevent the structural relaxation during cooling. B K-edge XANES spectroscopy was performed with ultra-soft x-ray, which is available at BL-2 in SR center, Ritsumeikan University. Fluorescence yield mode was adopted for the present measurement. The photoelectron from the glass sample was detected with the micro-channel plate placed at 90° direction for the x-ray irradiated.

3. Results and Discussion

The example of B K-edge XANES spectrum collected in this study is shown in Fig. 1. It

has been reported that the B K-edge XANES spectrum of alkali borosilicate glasses consists of five components, which can be categorized to three group as A, B and C as shown with dashed lines in Fig. 1. According to the previous study[1], the peak A, B and C can be attributed to 3-coordinated ($B^{[3]}$), 4-coordinanated boron ($B^{[4]}$) and their mixture, respectively. The proportion of $B^{[4]}$ can be derived by following relationship using the integration intensity of the peaks A, B_1 and B_2

$$B^{[4]} = (B_1 + B_2) / (A + B_1 + B_2).$$

The change in proportion of $B^{[4]}$ and $B^{[3]}$ with the heat-treatment temperature is shown in Fig. 2. The proportion of $B^{[3]}$ increased with temperature. In general, the formation of $B^{[3]}$ can be interpreted with below structural change.

$$BO_4 \rightleftarrows BO_3 + NBO$$

The present result indicates that the glasses undergone the treatment with higher temperature include larger amount of *NBO*. The coordination of boron at 550°C is consistent with the previous study by ^{11}B MAS NMR [2], and obviously demonstrates the usability of XANES spectroscopy for the detection of the coordination state of boron in glass.

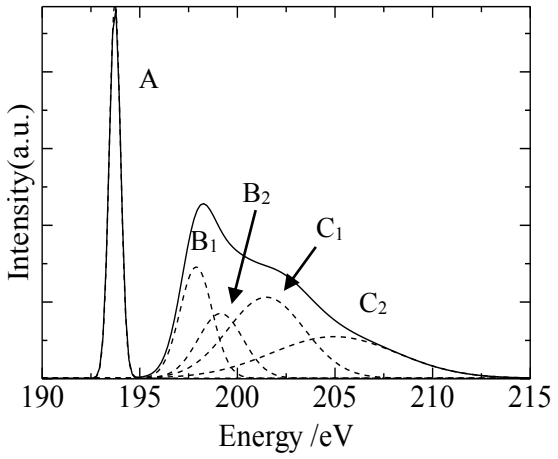

Fig. 1 Example of the XANES spectrum (treated at 550°C) and the peak assignments for the present glass

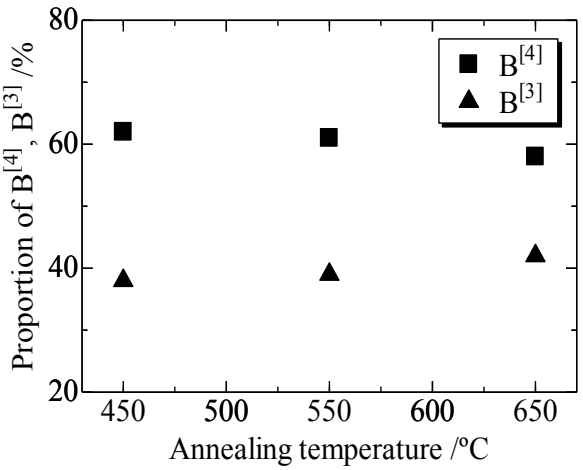

Fig. 2 Change in proportion of $B^{[3]}$ and $B^{[4]}$ with annealing temperature

References

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