Boron K-edge X-ray Absorption and Emission Spectroscopy Studies of Sodium Borate Glasses

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INTRODUCTION

When in binary alkali borate glasses (R_2O-B_2O_3, R : alkali metal) various physical properties such as the thermal expansion coefficient are plotted against the molar ratio of R_2O, they show the minimum or maximum value at about 20 mol% of R_2O. This phenomenon is well known as the 'borate anomaly' in glass science [1, 2] and discussed experimentally and theoretically from the standpoint of the glass structure. Several spectroscopic techniques including NMR [3-5], infrared absorption [6], and Raman scattering [7] have determined the proportion of two important structural units of boron atom; three-fold boron atom (B^3) coordinated trigonally with three oxygen atoms and four-fold boron atom (B^4) coordinated tetrahedrally with four oxygen atoms. The change in the proportion of B^4 to the total B^3 plus B^4 as a function of R_2O is closely related to the borate anomaly.

Recently, the quantitative analysis of B^3 and B^4 in R_2O-B_2O_3-SiO_2 and K_2O-SiO_2-B_2O_3-P_2O_5 glasses has been done by means of B K-edge X-ray absorption spectroscopy [8-10]. The valence band structure and the local structure for various oxide glasses have been investigated by means of XPS (X-ray Photoelectron Spectroscopy) [11]. We have measured XANES (X-ray Absorption Near Edge Structure) and XPS for xNa_2O-$(100-x)B_2O_3$ (x = 0~35) glasses [12].

In this work, xNa_2O-$(100-x)B_2O_3$ glasses and $Na_2B_4O_7$ crystal were investigated by means of excitation energy-dependent XES (X-ray Emission Spectroscopy) by using B.L. (BeamLine) 8.0.1 at ALS (Advanced Light Source).

EXPERIMENTAL

Glasses of the system xNa_2O-$(100-x)B_2O_3$ (x=25, 30, 35) were prepared using reagent grade powders (Na_2CO_3, B_2O_3). The batches were mixed and then melted in an electric furnace at 1100~1200℃ for 1 hour. The melts were quenched between two stainless steel plates to obtain glasses. $Na_2B_4O_7$ crystal was commercially purchased. All the glass and crystal samples were checked by X-ray powder diffraction.

Excitation energy-dependent XES near the B K-edge for these glasses and crystal was performed using B.L. 8.0.1 at ALS in Lawrence Berkeley National Laboratory. A 1500 groove/mm grating with the radius of curvature of 10 m was used.

RESULTS

B K absorption spectra for Na_2O-B_2O_3 glasses and $Na_2B_4O_7$ crystal measured by means of the fluorescence yield in order to determine the excitation energy are shown in Figure 1. The spectra agreed with the previously obtained spectra that we measured by means of the total electron yield using beam line 2 at the compact synchrotron radiation facility at Ritsumeikan University

[12]. In all the spectra, there are a sharp and strong peak at 193 eV and a broad structure from 195 to 208 eV. The peak is assigned to the transition of B 1s to p_π* in B^3 with the sp^2 hybridization and the broad structure is attributed to the transitions from B 1s to p_σ* in B^3 and B^4 with the sp^2 and sp^3 hybridizations, respectively. The numbers shown in the top spectrum are the excitation energies for measuring boron K X-ray emission spectra.

B K X-ray emission spectra for Na_2O-B_2O_3 glasses and $Na_2B_4O_7$ crystal are shown in Figure 2. The excitation energy dependence of the B K X-ray emission spectra of bulk B_2O_3 crystal has been reported previously [13]. A main peak around 182 eV can be ascribed to B 2p of both B^3 and B^4, and a weak low-energy satellite at 167 eV to hybridized B 2p and O 2s. Both the main peak and the satellite shift to lower energies with π* excitation of B^3 at 194 eV. A shoulder at 186 eV which can be assigned to the overlapped B 2p of B^3 and B^4 increases in intensity with σ* excitation of B^4 at 197-200 eV. The fact that the 186 eV shoulder observed in B_2O_3 crystal [13] is weak compared to those of these glasses shows the great contribution of B 2p of B^4 to the shoulders of these glasses. In future, it will be necessary to assign each peak in the obtained spectra by means of the molecular orbital calculations.

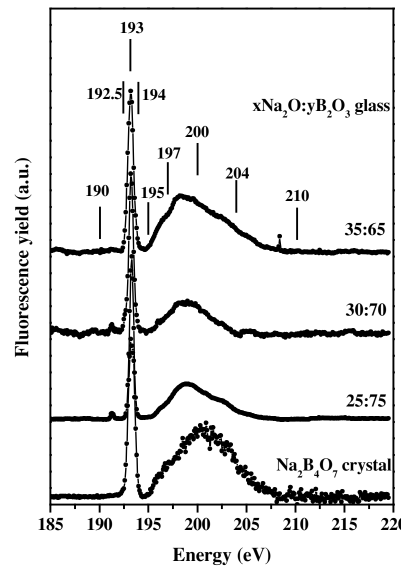
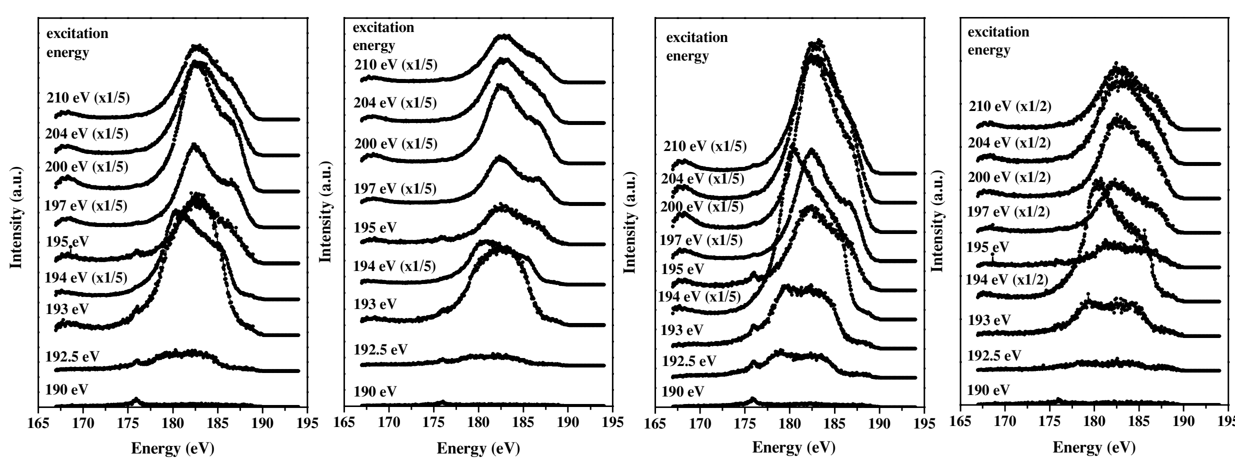


Figure 1. B K absorption spectra by means of the fluorescence yield for Na_2O-B_2O_3 glasses and $Na_2B_4O_7$ crystal.



(a) $35Na_2O$-$65B_2O_3$ (b) $30Na_2O$-$70B_2O_3$ (c) $25Na_2O$-$75B_2O_3$ (d) $Na_2B_4O_7$

Figure 2. Excitation energy dependent X-ray emission spectra for xNa_2O-$(100-x)B_2O_3$ glasses (x=25, 30, 35) and $Na_2B_4O_7$ crystal.

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