Investigation of local structural changes of several atoms constituting phosphosilicate and aluminoborate glasses by means of X-ray absorption spectroscopy

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Local structures around Si, P, Al, B and Ba atoms were elucidated by X-ray absorption spectroscopy (XAS) in phosphosilicate and aluminoborate glasses. For Si K-edge XAS experiments, BL-3 XAS beamline was constructed at SR center in Ritsumeikan University. The photon flux and energy resolution at BL-3 were estimated from XAS spectra of several standard samples. The photon flux at 2 keV is one order of magnitude larger than that of BL-4 XAFS beamline at the SR center.

6- and 4-coordinated Si atoms ($^{[6]}$Si and $^{[4]}$Si) were observed in alkali phosphosilicate glasses. The fraction of $^{[6]}$Si depended on the concentration of alkali oxide and P_2O_5. The maximum values were found at 20 mol% of alkali oxide x in $xR_2O \cdot (100\text{-}x)(0.2SiO_2 \cdot 0.8P_2O_5)$ {R=Li, Na, K} and at 0.9 mol% of P_2O_5 y in $25R_2O \cdot 75[(1.0\text{-}y)SiO_2 \cdot yP_2O_5]$ {R=Li, Na, K}. The Si-O interatomic distance changed from 1.63 to 1.79 Å with increasing the fraction of $^{[6]}$Si. Especially in the glasses with high content of $^{[6]}$Si, the Si-O interatomic distance was virtually the same as that (1.78 Å) in SiP_2O_7 involving $^{[6]}$Si. On the other hand, the local structure around P atoms remained unchanged.

In B K-edge X-ray absorption near edge structure (XANES) spectra of lithium borate glasses, a sharp peak was observed at 194.6 eV, which was assigned to the transition from the 1s to $p\pi^*$ states. The position, intensity and full width of half maxima of the peaks showed extrema with increase of the concentration of Li_2O. This indicates that the local structure around B atoms first changed from 3- to 4-coordination with increase of the concentration of Li_2O and changed again from 4- to 3-coordination with further increase of Li_2O.

In barium borate and barium aluminoborate glasses, local structures around B and Ba atoms changed with increase of both BaO and Al_2O_3 concentrations. The coordination number of B atom changed from 3 to 4 with increase of BaO concentration, and changed again from 4 to 3 with further increase of BaO. With increase of the BaO concentration, the local structures around Ba atoms changed from 6-coordination with one Ba-O bond length to 7～8-coordination with two Ba-O bond distances. The Ba-O interatomic distances were 2.77 Å in 6-coordination and 2.68 Å and 2.90 Å in 7～8-coordination. With increase of the Al_2O_3 concentration, the coordination number of B atom changed from 4 to 3, the coordination number of Al atom changed from 4 to 6, and local structures around Ba atom changed from 7～8-coordination to 4-coordination.