ESRF	**Experiment title: Boron coordination change between glasses and melts by IXS**	**Experiment number**: HD-490
Beamline: ID16	**Date of experiment**: from: 02/02/2011 to: 08/02/2011	**Date of report**: 29/08/2012
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Report:

The alkali borate glassy system is peculiar as the short range order around the network forming element (boron) can be modified with temperature. A partial conversion of BO_4 tetrahedra to BO_3 triangles with increasing temperature has been reported by ^{11}B NMR[1], Raman[2,3] and neutron diffraction[4] studies. However, none of these techniques can give quantitative determination of this boron coordination change. NMR measurements are difficult due to averaging of the two isotropic shifts of BO_4 and BO_3 in the liquids. Evaluation with Raman is assessed through bands that are indirectly associated with BO_4. Finally neutron diffraction is limited at high temperature due to thermal disorder that reduces the resolution required to separate the $^{[3]}$B-O and $^{[4]}$B-O distances. Recently, it was shown that inelastic X-ray scattering (IXS) can be used to obtain B K-edge XANES spectra[5]. In the XANES spectra, an intense and sharp feature near 194 eV (π* peak) is characteristic uniquely of BO_3 units. The $^{[3]}$B fraction is determined by calculating the ratio of the area under the π* peak to the total area from 190 to 210 eV (that includes $^{[3]}$B + $^{[4]}$B information), and setting the fraction to 100% for pure B_2O_3 glass at ambient temperature[5].

We have performed an X-ray Raman scattering experiment on ID 16 on lithium borate glasses as a function of temperature in order to access both the oxygen and the boron K-edges. The heating device was the aerodynamic levitation setup and laser heating developed at ID16 by the CEMHTI in Orleans. Three different glasses were measured with the following molar compositions: Li_2O-xB_2O_3, where x = 2, 3, and 9 denoted as LB2, LB3 and LB9, respectively. Figure 1(a) shows the boron *K*-edge IXS spectra for LB2, LB3, LB9 and B_2O_3 glasses at room temperature. Upon the addition of lithium oxide, the B *K*-edge spectrum is clearly modified with the appearance of a new absorption band around 198-200 eV and the intensity decrease at 194 eV, which is indicative of a gradual boron coordination change from $^{[3]}$B to $^{[4]}$B. By using the method previously described, we found that the number of BO_3 units decreases linearly from 100% in pure B_2O_3 to reach about 50% in LB2 at room temperature. Figure 2 shows the evolution of B K-edge

IXS spectrum as a function of temperature for LB2 and LB3 samples using the levitation device. The quality of data is excellent and allows the determination of the BO_3 proportion as a function of temperature. LB2 and LB3 shows the same type of behavior, *i.e.* a slight increase of the main peak at 194 eV accompanied by a shift of the broad band from 200 eV to 203 eV related to a partial conversion of BO_4 tetrahedra to BO_3 triangles. The proportion of BO_3 units increases from 50% at RT to 75-80% at 700°C for LB2 and from 60% to about 80% for LB3.

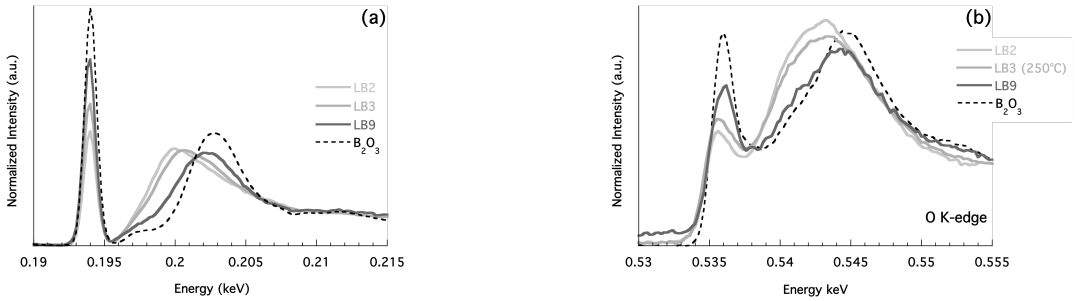

Figure 1: (a) Effect of lithium content on both (a) the B K-edge and (b) the O K-edge IXS spectra of LB2, LB3, LB9 and B_2O_3 glasses measured at room temperature at the exclusion of the O K-edge spectrum of LB3 which has been measured at 250°C.

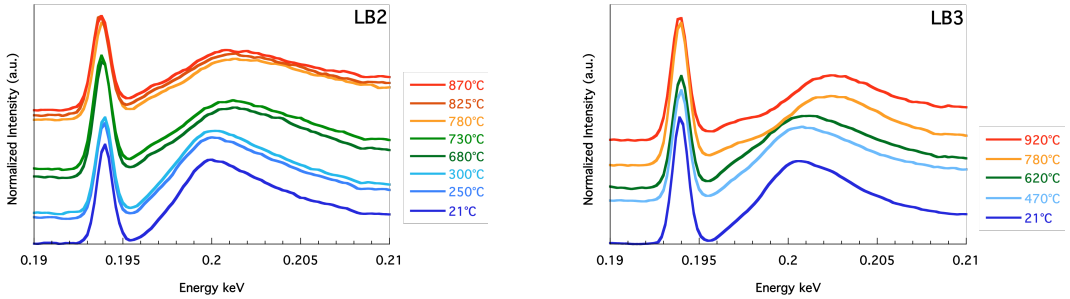

Figure 2: B K-edge IXS spectra of LB2 and LB3 glasses as a function of temperature.

In conclusion, the different lithium borate samples clearly show a BO_4 tetrahedra to BO_3 triangles conversion when heated. IXS combined with the aerodynamic levitation setup gives data of excellent quality, which allows to quantify the proportion of BO_3 units as a function of temperature. Our quantitative analysis was based on the assumption that the B K-edge spectrum of v-B_2O_3 is temperature independent. However, we discovered that this is not the case even at low temperature, meaning that the quantification of $^{[3]}$B is probably underestimated especially at high-temperature. Further investigations are then needed to disentangle this question.

References

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