

Boron *K*-edge XANES Studies of:

1) Borosilicate Glasses Proposed as Nuclear Waste Encapsulation Materials

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2) The dependence of the BO_3/BO_4 ratio on iron redox in iron rich sodium borosilicate glasses

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Introduction

Borosilicate glasses have been extensively investigated in materials sciences for their chemical, electrical and optical properties, and in environmental sciences due to their high chemical durability. They have been proposed both in Europe (France, United Kingdom and Germany) and the United States as candidate encapsulation materials for the storage of high-level nuclear waste. A robust assessment of the long-term stability of these glasses relies

on the knowledge of alkali borosilicate glass structure due to the importance of the structural control on physico-chemical properties of glasses.

Science

In the field of glass structural studies, alkali borosilicate system glasses present a challenge. Their structure is complex (Figure 1) because they have two network-formers, silicon (Si) and boron (B) and, in addition, boron has two possible coordination states, $^{[3]}B$ (where B is 3-fold coordinated) and $^{[4]}B$ (where B is 4-fold coordinated).

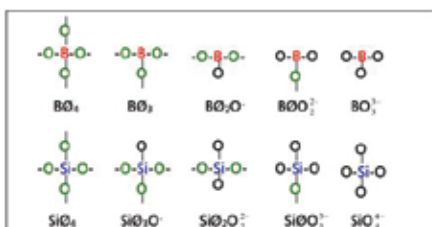


Figure 1. Basic structural units (top), [1] and possible super-structures (bottom) [2] in borosilicate glasses.

Furthermore, the ratio of $^{[3]}B/^{[4]}B$ in alkali borosilicate glasses is an important indicator of the alkali activity as the alkali ions prefer to associate with tetrahedral B. Consequently we can use this ratio as a parameter for estimating the relative stability of the glasses.

Discussion

Borosilicate glasses proposed as nuclear waste encapsulation materials

We have collected B *K*-edge XANES spectra for a series of sodium borosilicate ($Na_2O-B_2O_3-SiO_2$) and potassium borosilicate ($K_2O-B_2O_3-SiO_2$) glasses. Samples are prepared with different R and K ratios (where R is the ratio of alkali oxide to B_2O_3) and K (ratio of SiO_2 to B_2O_3). Furthermore, several selected reference samples (i.e. the borate mineral danburite) have been run after a variety of preparation methods. This is because there appears to be some change in the B coordination as a result of sample preparation. In particular it is strongly dependent upon whether or not the sample is crushed or ground. Our samples are therefore prepared as fresh fracture surfaces on single glass chips. The B coordination is then determined using a curve fitting procedure similar to [3]. However, we remove an arctangent background function (Figure 2a) followed by curve fitting (Figure 2b). The B ratios determined from the peak areas appear to be consistent with nominal $^{[3]}B/^{[4]}B$ ratios and ^{11}B NMR data.

The dependence of the BO_3/BO_4 ratio on iron redox in iron rich sodium borosilicate glasses

The aim of this experiment was to obtain quantitative information on changes in the BO_3/BO_4 ratio in iron rich sodium borosilicate glasses as a function of the iron redox state. In silicate glasses iron occurs in two different valence states, Fe^{2+} and Fe^{3+} . Fe^{3+} can occur as a network former in tetrahedral coordination and as a network modifier in octahedral coordination while Fe^{2+} can occur as a network modifier in octahedral coordination. Consequently the coordination state of Fe can have a significant influence on the structure of the silicate network. In addition, if the Fe acts as a charge compensator, it can induce changes in the local structure of boron. We investigated a series of sodium borosilicate glasses (67 mol % SiO_2 , 18 mol % B_2O_3 , 15 mol % Na_2O) to which were added 1, 5 and 10 mol % of iron as FeO. The resulting

glasses were equilibrated under different oxygen fugacities to ensure different redox ratios (ideally from the most reduced to the most oxidized state). Like the borosilicate glasses above, bulk samples were used for all experimental runs.

Conclusion

Analysis of the results obtained from the experiments above is currently underway. However, it is clear that determination of quantitative B coordination numbers using B *K*-edge XANES is not as straightforward as previously suggested. The B coordination is susceptible to changes as a result of sample preparation. In particular, grinding or crushing of samples (rather than exposure to air) may strongly modify the nominal B ratios in mineral standards. Spectra must be collected on freshly fractured surfaces immediately prior to insertion in the vacuum chamber. Furthermore, curve fitting of spectra is required to extract quantitative B ratios from mixed coordination samples. However, correct background removal is also a necessary requirement. Our data analysis indicates that the best removal procedure is fitting of an arctangent centred at ~205 eV and where the slope of the arctangent curve matches the slope of the experimental spectrum in this region. The experimental spectrum to the high energy side of the arctangent centre point must also be fit with an exponential curve that passes through the centre of the data points (Figure 2). Finally, preliminary analysis of the data also indicates that the spectra contain features that appear to be related to distortion of the B sites. We are currently investigating this relationship.

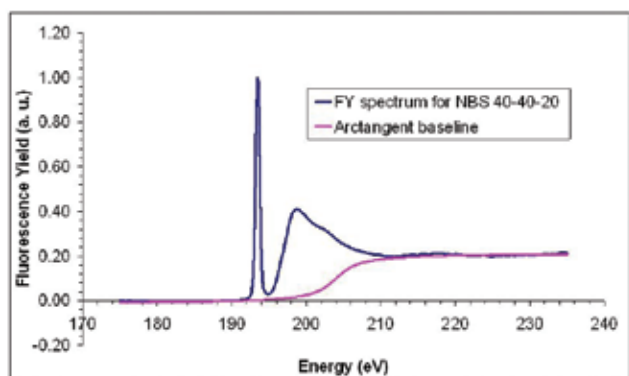
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a)



b)

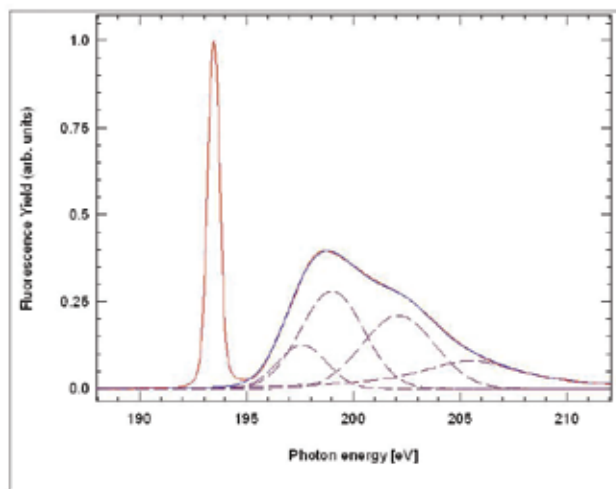


Figure 2. a) Plot of background removal b) Initial curvefit of high energy envelope of the same glass. Note that the highest energy fitted curve requires additional refinement.