

The Chemical Structure of Boron Oxide Species at Melt-Derived Glass Fibre Surfaces

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Introduction

This study aims to illustrate the effects of melt-derived glass fibre formation on the resulting surface chemical structure. While changes in glass composition and thermal history are known to affect average bond length and structural features such as non-bridging oxygen, most glass-formers (Si, Al, etc.) do not change coordination. Boron oxide, however, is known to change coordination states (between 3- and 4- fold geometries) with changes in thermal history and composition. While the behavior of

boron-oxide has been followed in the bulk by NMR, its behavior at surfaces is not known.

The local chemical structure of boron in bulk borosilicate glasses has been studied for some time by Nuclear Magnetic Resonance (NMR), Fourier Transfer Infrared (FTIR), and Raman analyses. None of these techniques, however, are inherently surface-sensitive and thus the corresponding local chemical structures for boron at multicomponent glass surfaces have not been directly characterized. Here we present the application of Near-Edge X-ray Absorption Fine Structure (NEXAFS) to pristine fiberglass surfaces to determine the coordination of boron atoms at the surface and near-surface regions. This surface structure data is supported by bulk structure by NMR and composition by X-ray Photoelectron Spectroscopy (XPS).

Science

Fleet and Muthupari have reported using NEXAFS to measure the coordination of boron at bulk glass fracture surfaces. [1] While their study was limited to alkali borosilicate glasses with 10-50% boron oxide, the technique can measure smaller concentrations given sufficient X-ray flux and integration time.

The compositions used in this study were chosen to illustrate changes in surface structure from fiberization of glasses containing: (1) typical commercial boron oxide concentrations and (2) the extremes of mostly 3- or mostly 4-coordinated boron. First, an alkali-free boroaluminosilicate was chosen to show boron in mostly 3-fold coordination, and had a nominal composition (in mole percent) of 58% SiO₂, 8% Al₂O₃, 5% B₂O₃, 1% Na₂O, 25% CaO, and 3% MgO. Second, a sodium-boroaluminosilicate was chosen to show boron in mostly 4-fold coordination, and had a nominal composition (in mole percent) of 67% SiO₂, 1% Al₂O₃, 6% B₂O₃, 16% Na₂O, 5% CaO and 5% MgO.

These bulk glasses were drawn into continuous fibres by remelting in a single-tip platinum bushing and attenuating at speeds up to 2.5 m/s. The resulting fibre diameters ranged from 4 to 25 μm (as measured from SEM images).

The surface composition of the as-drawn fibres was measured and compared to bulk glass vacuum-fracture surfaces. The XPS results showed that the fibre surfaces of both compositions were enriched in alkali relative to the bulk composition.

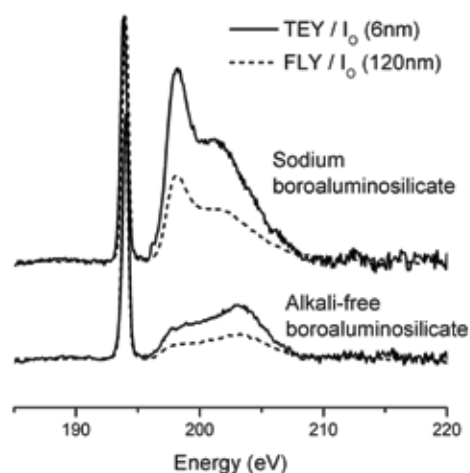
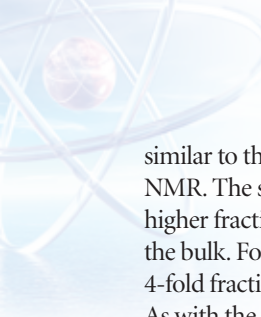


Figure 1: B K-edge NEXAFS spectra for alkali-free and sodium-boroaluminosilicate glass fibre surfaces. All spectra have been normalized to the intensity of the 3-fold peak at 194 eV, and offset for clarity. The peak at 198 eV is due to 4-fold boron, while the peak at 202-204 eV has contributions from both 3- and 4-fold boron. The TEY spectra (solid) represent boron in the topmost 6 nm whereas the FLY spectra (dashed) represent boron in the topmost 120 nm.

The coordination of the boron present in the bulk glass as well as throughout the fibre bulk was measured by solid-state ¹¹B MAS-NMR. The alkali-free boroaluminosilicate samples contained 16-24% 4-fold boron, with the highest fractions corresponding to slowly cooled samples. Similarly, the sodium boroaluminosilicate glass samples contained 56-65% boron in 4-fold coordination and up to 74% for well-annealed bulk samples.

The NEXAFS experiments were performed at the VLS-PGM beamline 11ID-2. The B K-edge spectra covered the photon range of 180-220 eV with a resolution of 0.1 eV. Total electron yield (TEY) and fluorescence yield (FLY) spectra were collected simultaneously. At these energies, the sampling depth for TEY was approximately 6 nm, and 120 nm for FLY.

The NEXAFS results in Figure 1 show that the fraction of 4-fold boron in the topmost 120 nm of alkali-free fibres is very



similar to that present throughout the fibre as measured by NMR. The surface of these fibres (by TEY) contained a much higher fraction of 4-fold boron than that which was present in the bulk. For sodium-boroaluminosilicate glass fibres, the FLY 4-fold fraction was slightly lower than that measured by NMR. As with the alkali-free fibres, the surface (by TEY) contained a much higher fraction of 4-fold boron than was measured in the bulk.

Discussion

Melt-derived borosilicate surfaces have been purported to be enriched in boron with 3-fold coordination owing to its unique geometry and low surface tension.[2] However, these results show that rapidly-quenched fibre surfaces contain both coordination states. In fact, surfaces of both low- and high-alkali glasses contain higher fractions of 4-fold boron than is present in the bulk. This finding is likely due to increased surface alkali from diffusion during fiberization and reaction with environmental species such as water, both of which may act to stabilize the 4-fold coordination.

Conclusion

B K-edge NEXAFS is a powerful method for understanding the chemical structure of multicomponent glass surfaces. Here, melt-derived surfaces were shown to contain a higher fraction of 4-fold boron than was present in the bulk. This is likely due to both increased alkali concentration at these surfaces, and adsorption of water from the surrounding environment. Additional work will focus on organic- and organosilane adsorbates and their impact upon the boron coordination at these surfaces.

References

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