Earth and Environmental Science

Oxygen *K*-edge and Titanium *L*-edge XANES Studies of Glasses and Minerals

G.S. Henderson, S. Dong (1), B. Cochain (2), D.R. Neuville (2), T. Hoche (3)

(1) University of Toronto
(2) Physique des Minéraux et Magmas, CNRS-IPGP, Paris, France
(3) Leibniz-Institut für Oberflächenmodifizierung, Leipzig, Germany

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PRINCIPAL CONTACT:

Grant S Henderson
Geology Department
University of Toronto
henders@geology.utoronto.ca
Phone (416) 978-6041

Introduction

Glasses are amorphous solids that exhibit the glass transition (c.f. [1]). They are used widely in a number of commercial applications from fibre optics to the storage of nuclear waste. Earth scientists are interested in glasses as proxies for silicate melts which play a critical role in determining the physical behaviour of magmas and, in turn, igneous processes such as flow of lava and volcanic eruptive style. While *in situ* studies of melts are most desirable, it is easier to use quenched melts or glasses as analogues. This is because glasses are considered to have structures that resemble the liquid state, and since they are solid, experimental data can be extracted more easily (e.g., at room temperature) than from molten analogues. We have been using O *K*-edge XANES to probe the structural environment surrounding the O atoms in germanate ([2, 3]), germanophosphate [4] and calcium aluminosilicate glasses [5, 6].

More recently we have also begun to investigate the surface structure of fresnoite ($Ba_2TiSi_2O_8$) composition glasses and crystalline phases (the latter are incommensurate phases that exhibit long-range modulations in their structure) after amorphization with argon ion beams. We are particularly interested in the coordination of Ti and whether or not the surface structure of these phases differs from the bulk structure.

Science

The O *K*-edge XANES has proven useful in studying cation coordination when other techniques have not been suitable. XANES spectral features are due to electronic transitions between O *1s* to O *2p* anti-bonding states, which are mixed with cation orbitals [7]. This mixing makes the O *K*-edge XANES sensitive to the atomic environment of the cation. Numerical modeling of the O *K*-edge XANES spectra of crystalline germanate phases used as standards for analysis of the glass spectra, clearly show a relationship between XANES peaks and the cation to which the oxygen is bound [8]. We have used this relationship to study the germanophosphate and calcium aluminosilicate systems (CAS).

Ti *L*-edge XANES is also useful for determining the coordination of Ti [9]. Distinct *L*-edge spectra are obtained depending upon whether or not Ti is 4-, 5-, or 6-fold coordinated. We use this approach to investigate a series of fresnoite glasses and single crystals after exposure to different intensity ion beams. Furthermore, we have applied different thickness thin films of Ir or Cr to the sample surfaces as a means to attenuate the escape depth of the electrons and hence to depth profile the samples.

Discussion

Germanophosphate Glasses

These glasses also exhibit a germanate anomaly similar to the alkali germanate glasses [10]. One possible explanation for this anomalous behaviour is changes in Ge coordination. Unfortunately, attempts to determine the Ge coordination have been unsuccessful except from circumstantial evidence. However, using the numerical results we are able to determine that the shift in the O *K*-edge XANES peak at around 538 eV (Figure 1) is due to an oxygen that is shared between a Ge atom in 4 fold coordination and one in 5-fold coordination.

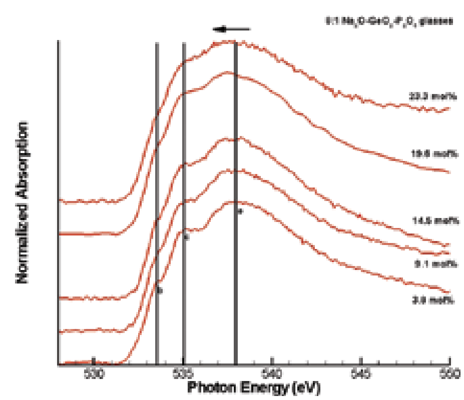

Figure 1. O K-edge XANES spectra of Na_2O germanophosphate glasses with 8:1 GeO_2:P_2O_5 ratio (after [4])

Calcium aluminosilicate (CAS) glasses

These glasses are highly refractory and have excellent optical and mechanical properties ([11] and references therein). Furthermore, glasses in this system can be made by conventional melt quenching techniques in a narrow range of compositions (30–70 mol% CaO) at very low SiO_2 contents, contrary to alkali or Mg aluminosilicate glasses. Addition of small amounts of SiO_2 to CaO–Al_2O_3 (CA) glasses extends the glass-forming region and decreases the liquidus temperature. However, the macroscopic properties are markedly changed with the introduction of silica indicating changes in their structure.

The O *K*-edge spectra are very complex and contain features resulting from mixing of the oxygen orbitals with both Ca and Al. In addition, contributions from bridging (BO) and non-bridging oxygens (NBO) can also be distinguished.

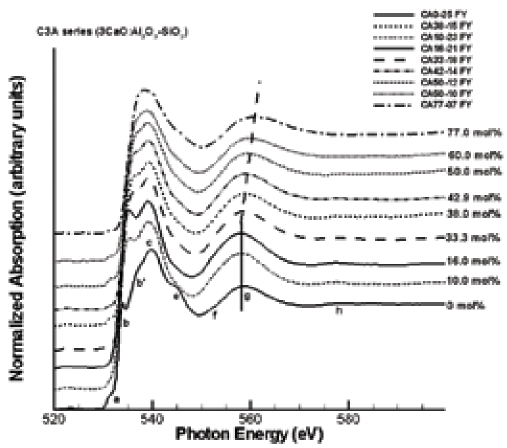

Figure 2. O K-edge XANES spectra for a series of glasses along the join $3CaO\text{-}Al_2O_3\text{-}SiO_2$. The SiO_2 content of each composition is plotted. There is a clear structural change around 33 mol% SiO_2 which is related to the Q speciation and Ca coordination in the glasses (cf., [6]).

Ion beam amorphized fresnoite glasses and crystals.

While analysis of the data recently collected on the SGM is ongoing, preliminary results clearly show differences in the Ti *L*-edge XANES (Figure 3). This behaviour is consistent with [12] who have predicted that the structure of a glass near its surface could be different from that of the bulk.

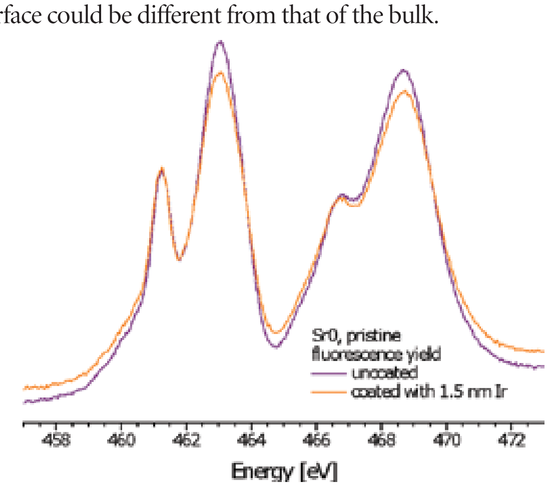

Figure 3. Ti *L*-edge XANES spectra of Sr fresnoite glass with and without an Ir thin film. Clearly there are differences between the spectra for the high energy peaks in both the L_3 and L_2 edges. The spectrum of the sample with the thin film reflects structure closer to the surface than the sample with no thin film.

Conclusion

The O *K*-edge is useful for probing the structural environment of cations bound to oxygen. In the CAS system features due to differing Ca coordination environments, as well as, whether or not Al is attached to a BO or NBO can be also distinguished. In germanophosphate glasses energy shifts in specific spectral features can be indirectly correlated with Ge coordination changes.

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