



Experiment Report Form



Beamline: BM29	Experiment title: Iron K-edge XANES and EXAFS of oxide glasses	Experiment number: HD 320
Shifts: 12	Date of experiment: from: 08:00 29/08/2008 to: 8:00 to 02/09/2008	Date of report: 18/04/2009 <i>Received at ESRF:</i>
Local contact(s): Olivier Mathon; Sakura Pascarelli		
Names and affiliations of applicants (* indicates experimentalists): Dr. Paul A. Bingham Mr. Oliver M. Hannant		

Report:

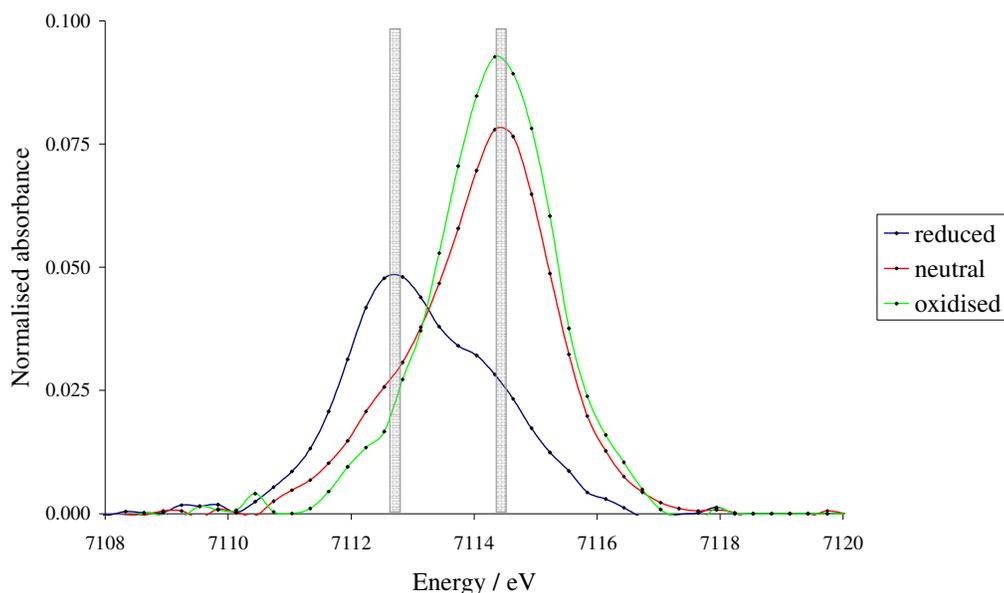
Iron is present at many different levels (0.1 – 20 mol % Fe₂O₃) in glasses resulting from the immobilization by vitrification of toxic and nuclear wastes. Its oxidation state and local structural environment in these glasses are very important because they influence physical properties, for example high temperature viscosity, crystallisation and chemical durability. It is commonly agreed that iron exists as a combination of Fe²⁺ and Fe³⁺ in the majority of oxide glasses, and that both oxidation states generally occupy a mixture of tetrahedral and octahedral sites. Our recent research has indicated, for the first time, selective medium-range ordering around Fe³⁺ cations in oxide glasses [1] and recent French research has suggested the presence of 5-coordinated Fe³⁺ cations in some oxide glasses [2]. Therefore there is still considerable debate surrounding the relationships between glass composition, preparation conditions and short-range and medium-range structure of iron in oxide glasses. Recent analyses by Mr. Oliver Hannant, one of my PhD students, have identified a new relationship inextricably linking iron oxidation states and coordination in oxide glasses [3], which we wished to explore and develop further. We had originally been allocated beam time at SRS Daresbury for this project but we lost all of our useful beam time due to a water leak inside the storage ring. Compensation time at Daresbury was not granted and operations there closed in Summer 2008. Fortunately we were able to secure precious beam time at ESRF: these Fe K-edge XAS studies constituted a major part of the final year PhD studies of Mr.

Hannant, therefore we are very grateful to our beamline contacts and to ESRF for granting us the beam time which was very successful.

High quality Fe K-edge XANES and EXAFS spectra were successfully obtained for a suite of simulated, inactive nuclear and toxic waste glasses and for several crystallographically well-defined standard materials. Spectra were acquired on beamline BM29 simultaneously in transmission and fluorescence modes between 7000 eV and 7850 eV. Powdered samples were prepared in the form of pressed pellets of sample mixed with BN to ensure appropriate edge steps were obtained. Iron foil was placed before the second ionization chamber to ensure that all spectra were supplied with a reference data channel. Measurements were carried out in air at room temperature, and several spectra were collected for each sample and summed to maximise signal-to-noise ratio especially at high k. The data obtained have enabled Mr. Hannant to successfully complete his PhD research and his thesis will be submitted for examination shortly.

Iron K-edge XAS spectra exhibit a characteristic pre-peak at 7111 – 7116 eV. An arctangent function was fitted to the Fe K-edge in order to remove its contribution and allow analysis of the pre-peak. Deconvolution of these pre-peaks (see Figure 1) allowed an assessment of the $\text{Fe}^{2+} / \text{Fe}^{3+}$ ratio (which gave good agreement with data obtained from Mössbauer spectroscopy) and also the average coordination. Plotting centroid position versus integrated pre-peak intensity and comparing it with those obtained for our standards and other published data confirmed an average coordination number for Fe^{2+} and Fe^{3+} of approximately 5 and 4.5, respectively. This can be interpreted either as the existence of discrete 5-coordinated sites or as a mixture of 4- and 6-coordinated sites.

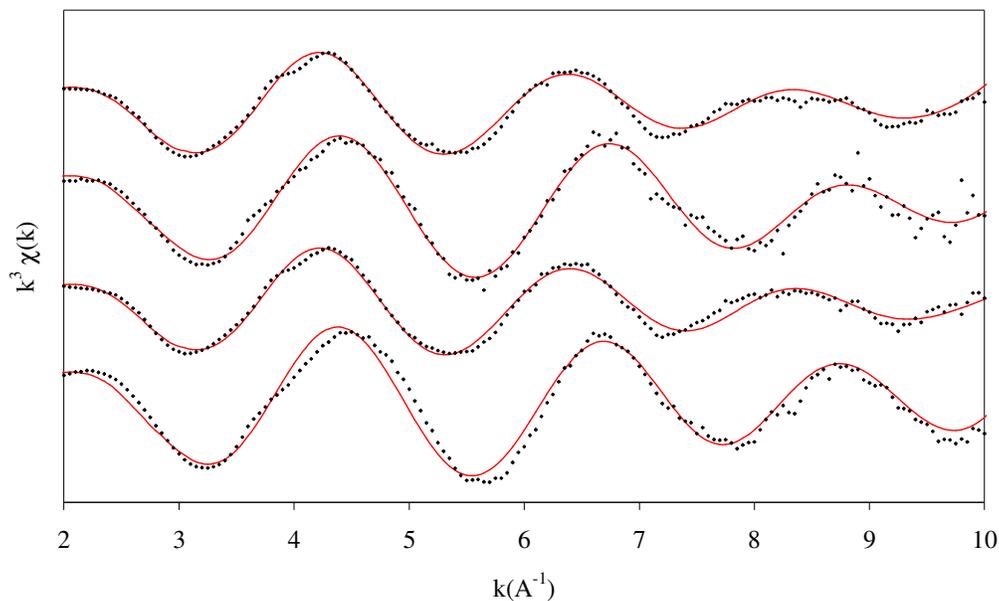
Figure 1. Deconvoluted pre-edge peaks for glasses prepared under different $p\text{O}_2$.



EXAFS analysis was carried out on spectra obtained for glass samples that were redox-pure (i.e. > 95% of Fe was Fe^{2+} or Fe^{3+}). Two glasses obtained by vitrifying water treatment wastes provided the following results (Figure 2): Fe^{3+} CN = 4.23, $d(\text{Fe-O}) = 1.89 \text{ \AA}$ with $\Delta\sigma^2 = 0.0081$; Fe^{2+} CN = 4.49, $d(\text{Fe-O}) = 1.98 \text{ \AA}$ with $\Delta\sigma^2 = 0.0121$. Further data processing is currently underway because the Fourier transformed spectrum may suggest the existence of

next-nearest-neighbour ordering around Fe^{3+} , which is consistent with our hypothesis based on our previous work on dilute iron glass systems [1]. We aim to complete this analysis and determine the nature of the next-nearest-neighbour cation shortly.

Figure 2. EXAFS (dotted) and fits (lines) for experimental glasses



Direct spectroscopic evidence for the existence of specific 5-coordinated Fe^{2+} or Fe^{3+} sites remains somewhat elusive: pre-peak centroid positions and integrated intensities are suggestive of 5-coordinated sites but a mixture of 4- and 6-coordinated sites can provide similar results. The same is true of the EXAFS that we have been able to obtain but nevertheless our results are encouraging. Further analysis and combinatorial fitting of XANES spectra against the data obtained for spectroscopic standards is also underway. Following completion of the work that is still in hand a paper will be prepared and submitted to an appropriate journal.

References

- [1] P. A. Bingham, J. M. Parker, T. M. Searle, I. Smith, *Journal of Non-Crystalline Solids* 353 (2007) 2479-2494.
- [2] C. Weigel, L. Cormier, L. Galois, G. Calas, D. Bowron, B. Beuneu, *Applied Physics Letters* 89 (2006) 141911.
- [3] O. M. Hannant, P. A. Bingham, S. D. Forder, R. J. Hand, *Physics and Chemistry of Glasses: European Journal of Glass Science and Technology B* 49 (2008) 27-32.