



	Experiment title: Ionizing irradiation effect in transition-metal bearing glasses of nuclear interest.	Experiment number: EC 395
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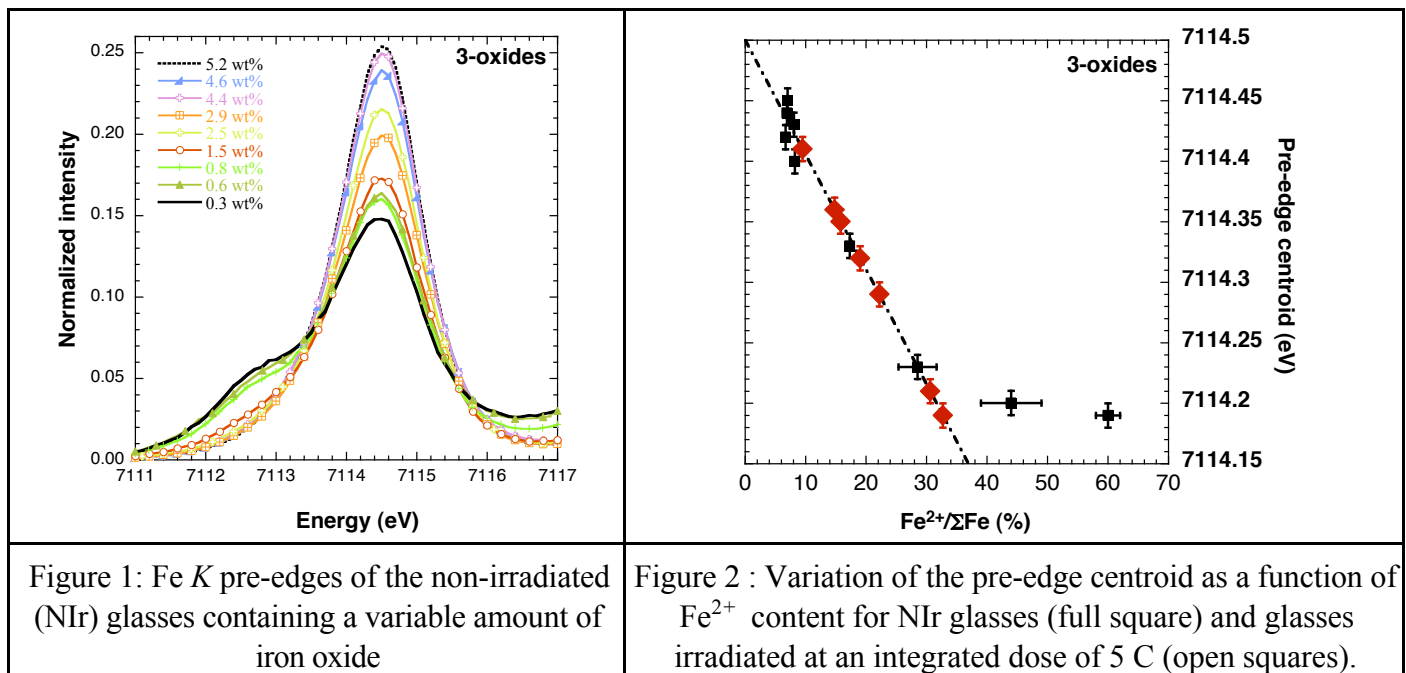
Report

Since July 2006, France has decided to include nuclear wastes in borosilicate glasses. Despite this political decision, important scientific issues remain unclear. One of these questions concerns the structural changes of the borosilicate matrix under irradiation and more specifically the alkaline migration that may enhance the glass weathering processes. Ionizing irradiation effects in oxide glasses are controlled by mobile species migration during irradiation. The alkaline migration in the glass leads to structural changes at a dose around 10^9 Gy (Boizot et al., 2005). One possible way to decrease the alkaline migration under ionising radiation consists in doping the oxide glass with transition metals (TM) like iron (Olivier et al., 2005). In that case, we have shown that the alkaline mobility under irradiation is controlled by defects precursor of the migration and that the defects produced at one integrated dose are decreasing as a function of the dopant concentration. We have analysed also reduction processes of Fe^{3+} ions correlated with the dose integrated into the sample by Electron Paramagnetic Resonance (EPR) and optical absorption spectroscopies. Moreover, changes in the coordination number of both Fe^{3+} and Fe^{2+} ions environments have been detected by optical absorption measurements. However, precise quantification of the reduction phenomenon and coordination number changes under ionizing radiation in these glasses cannot be determined from EPR and optical absorption measurements, and neither from Mössbauer spectroscopy. (too low Fe concentration and too small samples). The only data concerning precise relative proportion of iron in Fe^{2+} and Fe^{3+} oxidation states have been effected by wet chemistry in all iron doped glass compositions of this work. However, the oxidation state of the irradiated glasses cannot be determined by wet chemistry because of the destructive character of these methods.

The aim of the project was therefore to use a non-destructive method allowing a qualitative and

quantitative determination of the Fe oxidation state in both non-irradiated and irradiated glasses, to better understand the processes involved in the β -irradiation of glasses. During our allocated beamtime, high energy resolution fluorescence detected (HERFD) XANES experiments were performed on beamline ID26. Fe K edge spectra were recorded on two systems : $\text{SiO}_2\text{-Na}_2\text{O-CaO-Fe}_2\text{O}_3$ and $\text{SiO}_2\text{-Na}_2\text{O-ZrO}_2\text{-Al}_2\text{O}_3\text{-CaO-B}_2\text{O}_3\text{-Fe}_2\text{O}_3$. Each spectrum has been obtained by accumulating 3 spectra recorded between 7050 eV and 7300 eV, Additional spectra were recorded up to 7800 eV in order to properly normalize the spectra to the K edge jump. We recorded the Fe $K\alpha_1$ fluorescence line using the high-energy resolution spectrometer of the ID26 beamline (Ge(440) crystal analyzer). Well-resolved spectra were obtained for all our samples, which allowed a detailed analysis of the pre-edge to be done (Fig. 1 and 2).

The Fe oxidation state in the irradiated samples was determined using the pre-edge features as a function of the iron content, the glass composition and the dose integrated. The results of the $\text{SiO}_2\text{-Na}_2\text{O-CaO-Fe}_2\text{O}_3$ system are shown in this report (Fig. 1 and 2) to illustrate our results, since similar results have been obtained for the second series. Our results show that the shape and the energy of the centroid of pre-edge are modified with the Fe_2O_3 content, suggesting a modification of the Fe^{2+}/Fe ratio despite similar synthesis conditions. The variations of the pre-edge features also indicate that structural changes in the iron environment (geometry and coordination) occur concomitantly to oxidation state variations. The spectra obtained for the same glass series but irradiated with a 5C dose display modification of the pre-edge features with respect to those of non-irradiated samples, and they reveal a more important content in Fe^{2+} for the irradiated glasses. However, the strong variations observed for the amount in Fe^{2+} created under irradiation suggest the processes occurring during the irradiation seem more complex than a simple reduction of Fe^{3+} ions (Rossano et al. 2009).



References

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