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Oxidation state variation under β-irradiation in an iron-bearing soda lime glass system

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Abstract. The effect of ionizing radiation on glasses in the system SiO_2-CaO-Na_2O-Fe_2O_3 is investigated as a function of iron concentration or / and irradiation dose by a pre-edge analysis at the iron K-edge. While reduction phenomenon is clearly observed for large irradiation doses (5 C), the effect of irradiation for intermediate doses is more challenging to interpret. Comparison between X-ray absorption measurements, colorimetry results and Electron Paramagnetic Resonance measurements suggest that iron environment may be modified without the ions being reduced.

1. Introduction

Since July 2006, France has decided to immobilize nuclear wastes in glassy matrix. Despite this political decision, important scientific issues remain unclear. One of these questions concerns the alkaline migration that may enhance the glass weathering processes. One possible way to diminish this migration consists in doping the oxide glass with transition metals like iron. As the dopant concentration increases, a decrease of the number of defects has been observed [3, 11]. In order to obtain quantitative information on irradiation processes in glasses in the system SiO_2-Na_2O-CaO-Fe_2O_3, the measure of ferrous iron to total iron ratio as a function of the iron content and of the dose integrated have been performed using X-ray absorption Near-Edge Spectroscopy (XANES) measurements at the Fe K-edge (pre-edge analysis) combined with wet-chemistry results and Electron Paramagnetic Resonance (EPR) experiments.

2. Experimental details

Sample compositions are given in table 1. The sample irradiations were conducted using electrons generated by a van de Graaf accelerator operating at 2.5 MeV and 16 μA (Ecole Polytechnique, Palaiseau). Irradiation doses vary between 0 and 5 C. High energy resolution fluorescence detected (HERFD) XANES experiments were performed on beamline ID26 at the ESRF. The electron energy was 6.0 GeV with a ring current of 200 mA. The incident energy was selected by

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means of a pair of cryogenically cooled Si(311) single monochromator crystals. Higher harmonics were suppressed using two mirrors with a Si coating at 3 mrad.

Table 1. Elemental composition of glasses prepared following the procedures described in [11] (E3 to E9) or in [13] (E1 and E2) ; pre-edge centroid (δ) and $Fe^{2+}/\Sigma Fe$ (rr) for NIr samples and glasses irradiated at 5 C. rr for NIr glasses has been determined by wet chemistry. rr of Ir samples is deduced from the present study by correlating pre-edge shift and chemistry measurements on NIr samples.

Sample	Si wt%	Na wt%	Ca wt%	Fe_2O_3 wt%	δ_{NIr} (eV)	δ_{Ir} (eV)	rr_{NIr} %	rr_{Ir} %	Δrr %
E1	37.1	18.4	2.2	0.3	7114.19	-	60	-	-
E2	35.3	17.6	2.1	0.6	7114.20	-	44	-	-
E3	34.1	15.1	2.2	0.8	7114.23	7114.21	28.5	33.2	4.7
E4	34.7	14.7	2.0	1.5	7114.33	7114.19	17.3	35.5	18.2
E5	34.8	13.8	2.2	2.5	7114.40	7114.32	8.2	20.7	12.5
E6	33.1	15.5	1.9	2.9	7114.42	7114.29	6.7	24.1	17.4
E7	34.0	13.6	2.2	4.4	7114.43	7114.41	8.1	10.3	2.2
E8	31.6	15.4	2.2	4.6	7114.44	7114.35	6.9	17.2	10.3
E9	33.7	13.5	2.0	5.2	7114.45	7114.36	7.0	16.1	9.1

The analyzer used exploits the Bragg reflection of a 1m bending radius spherically bent crystal in the vertical Rowland geometry. Ge(440) was used for detecting the Fe $K\alpha_1$ emission line. We recorded the intensity variation of the $K\alpha_1$ (6.405 keV) and $K\alpha_2$ (6.392 keV) lines as a function of the incident energy to record high-resolution absorption spectra at the Fe K-edge (7.112 keV). The emitted photons were measured using an avalanche photodiode. The resolution of the spectrometer was 0.55 eV taken from the FWHM of the elastic peak. No off-diagonal signal was observed on the RIXS plane for the 4.6 wt% Fe_2O_3 glass ensuring that the HERFD spectra of glasses can be treated in the same way as standard XAS spectra [9]. The pre-edge region of normalized HERFD spectra was fitted using the fityk program [8]. Two Voigt Area functions (or three for the most reduced samples) were necessary to model the pre-edge and one Gaussian Area function to model the contribution of the main edge to the pre-edge feature. All contributions were fitted simultaneously. Pre-edge information was derived by calculating the area-weighted average of the Voigt function position (centroid). EPR measurements were conducted at 298 K and 100 K on a X band ($\nu = 9.420$ GHz) EMX Brücker spectrometer using a 100 kHz field modulation, 3 G of amplitude modulation and an applied microwave power of 10 mW. Spectra have been normalized to the receiver gain and to a 100 mg sample weight. Total iron and Fe^{2+}/Σ Fe have been determined by colorimetry on 50 mg of glass powder following the procedure described in [2].

3. Results and discussion

An initial series of non-irradiated (NIr) glasses containing a variable amount of iron oxide have been analyzed by XANES experiments at the Fe K-edge. The pre-edge region of the normalized HERFD spectra is shown in figure 1A.

As the Fe_2O_3 content increases, the shape of the pre-edge feature is modified and the pre-edge centroid (δ) is shifted toward higher energy (figure 1 and table 1). These variations indicate a modification of the Fe^{2+}/Σ Fe ratio (see [14] and references therein) despite similar synthesis conditions. The variation in the oxidation state is confirmed by colorimetry measurements (figure

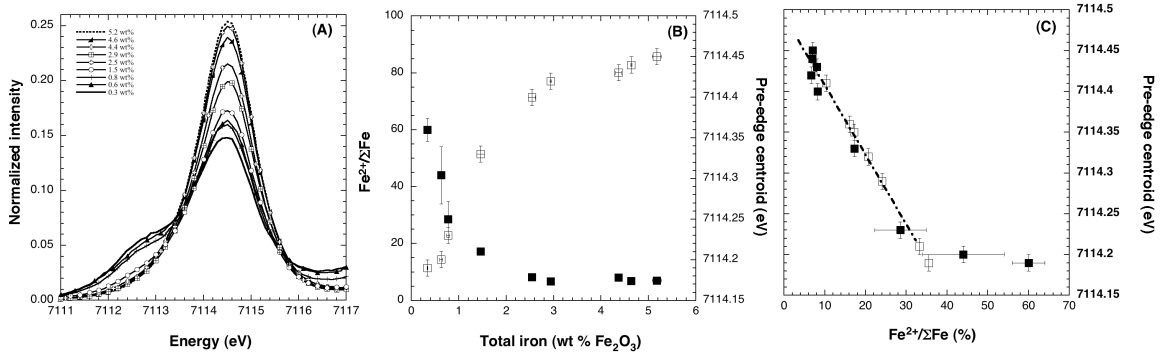

Figure 1. (A) Pre-edge region of normalized HERFD spectra for glasses with a variable amount of iron oxide. (B) Variations of pre-edge centroid (open square) and Fe^{2+} content (full square) as a function of total Fe concentration. (C) Variation of the pre-edge centroid as a function of Fe^{2+} content for NIr glasses (full square) and glasses irradiated at an integrated dose of 5 C (open squares).

1B). The lower the iron oxide content, the higher amount of Fe^{2+} in the glass in good agreement with a previous wet-chemistry study performed on sodo-lime silicate glasses [6]. The NIr glass series and the chemical measurements were used to build an empirical calibration curve between δ and rr values derived by chemistry (figure 1C). The correlation between δ and rr ratio appears to be linear for rr smaller than 30 %. For greater rr, δ is not sensitive to redox variations. This indicates that structural changes in the iron environment (geometry and coordination) occur concomitantly to oxidation state variation. Indeed for reduced glasses, and independently of the total iron content, it has been shown that two ferrous iron coordination distribution (4- and 5- or 6-fold coordinated Fe^{2+}) are present in glasses [1, 12]. In such a complex case (presence of different Fe^{2+} species), the experimental pre-edge is the average of the different contributions. Consequently, the understanding of the pre-edge centroid behaviour necessitates the knowledge of each individual signal.

The same glass series (except low-iron contents) has been β-irradiated with a 5 C dose. The pre-edge region is modified under irradiation (spectra not shown). Pre-edge centroids of irradiated (Ir) glasses are reported in table 1 and figure 1C. Using the previously determined calibration curve, rr of Ir samples may be estimated (table 1). Whatever the glass composition, Ir glasses appear to contain more Fe^{2+} that NIr glasses. However, although the irradiation dose is the same, the amount of Fe^{2+} created under irradiation strongly varies, between 2 and 18 %, suggesting that more complex processes than a simple reduction of Fe^{3+} ions occurs.

To investigate more precisely irradiation processes, the E8 glass, irradiated at different doses, was studied by XAS and EPR experiments (figure 2). At low irradiation doses, the intensity of the pre-edge feature is stronger than for the Nir glass one, while at higher doses, the intensity of the pre-edge decreases (figure 2A). Considering EPR measurements, features assigned to isolated Fe^{3+} iron (around 1500 G (g=4.3) and 3500 G (g = 2) [5, 10, 7]) are modified as irradiation dose increases (figure 2B and C). As colorimetry measurements do not evidence reduction processes, and because of the small variation in the pre-edge shape and intensity, these modifications have to be related to electronic interactions in the vicinity of Fe ions during irradiation processes. For doses lower than 1 C, The decrease of isolated Fe^{3+} EPR lines (figure 2B) can be explained by strong dipole dipole interaction between irradiation defects and Fe^{3+} ions.

The combined use of wet-chemistry, XAS and EPR measurements have allowed to shed light

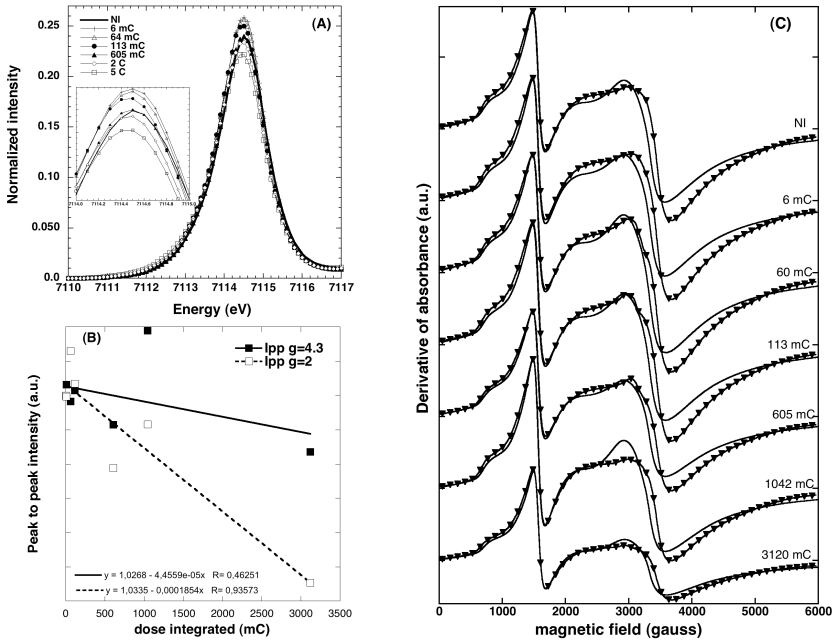

Figure 2. (A) Pre-edge features for the E8 glass β-irradiated at different doses. (B) Variation as a function of dose of the peak to peak intensity (Ipp) of the two isolated ferric iron lines normalized to NIr glass intensities.(C) EPR spectra recorded at room temperature (crosses) and 100 K (line) of E8 sample β-irradiated at different doses. Spectra integrated at one dose have been normalized to the Fe^{3+} EPR line at 1500 G.

on irradiation processes in glasses. At doses lower than 1 C, the decrease of ferric iron signal observed by EPR spectroscopy may be explained by dipolar interactions in ferric iron vicinity. At higher doses, iron-bearing glasses are reduced and the rate of reduction seems to vary as a function of total iron concentration.

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