

Direct Evidence for Trivalent Titanium in Artificially Irradiated (electrons) Oxide Glasses

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Abstract. Ti-doped borosilicate and disilicate glasses were irradiated with high-energetic electrons in order to study Ti(IV) reduction processes. Reduction efficiency was actually confirmed by an important Ti(III) EPR signal around $g=1.93$ in irradiated samples. The Ti(III) amount increases with the irradiation dose. Moreover, the Ti(III) environment depends on the glass composition. Hence, the reduction process efficiency is strongly correlated to the Ti(IV) environment in the pristine glass. The Ti environment was analyzed by Ti K-edge XANES in order to understand the reduction mechanisms. Pre-edge analysis of non-irradiated samples indicates the presence of four, five and six coordinated tetravalent Ti sites in borosilicate glasses, whereas in disilicate the Ti(IV) coordination is a mixture between five-fold and six-fold. In irradiated samples, the Ti pre-edge shows a slight low-energy shift associated to an intensity decrease in disilicate glasses. Correlation between EPR and XANES experiments allows for interpretation of the pre-edge variation in terms of Ti(III) formation. Profiles (μm resolution) were also performed to measure the proportion of Ti(III) on different points across the irradiated DS. No significant difference in XANES spectra was observed suggesting that the production of Ti(III) is homogeneous in the volume

Keywords: Ti XANES, glasses, irradiation, reduction

PACS: 61.10.Ht; 61.43.Fs; 61.80.Fe

INTRODUCTION

Multicomponent aluminoborosilicate glasses are presently the reference material for high level activity nuclear waste (HLAW) storage in many countries. Therefore, it is especially important to be able to predict the structural evolution of such material due to self-irradiation. Under sufficient ionizing irradiation, the glass structure is modified, particularly at doses higher than 10E^9 Gy [1]. We determined that structural modifications occurring under irradiation are mainly linked to the alkaline ions migration [2]. However, another phenomenon is observed; it concerns the reduction of some cations such transition ions (Fe(III), Cr(VI)) or rare earth element (Sm(III), Eu(III)) [3].

The present study is dedicated to Ti(IV) reduction processes in oxide glasses under electronic irradiation. One aim of this work is to understand the

precise mechanism; therefore several glass compositions are studied: disilicate and borosilicate doped with different Ti concentration and irradiated at a large dose range. In this study, irradiated glasses were first analyzed by EPR spectroscopy at 4K to characterize the expected Ti(III) signal around $g=1.93$. Then Ti-K edge X-ray near edge structure (XANES) was undertaken. As a matter of fact, previous Ti-K edge XANES studies showed their ability to provide information on the Ti(IV) local environment. Particularly, a high-resolution pre-edge analysis of Ti(IV) provides information on this cation symmetry but also on Ti’s coordination in some favorable cases as in oxide glasses [4]. We are interested in the present study in trying to correlate electron spin resonance (EPR) and XANES results in order to analyze irradiated glasses XANES spectra features.

EXPERIMENTAL

The Ti(IV) doped borosilicate (BS) and disilicate (DS) glasses were irradiated with 2 MeV electrons by using a Van de Graff accelerator (LSI, France) with doses ranging between 0 and 5 C. Pristine glasses were doped with 0.5, 1, 1.5 and 2% of TiO₂ (in wt %). DS2 means a Na disilicate glass doped with 2 mol. % of TiO₂.

The EPR spectra were obtained using a X band ($\nu = 9.48$ GHz) EMX Bruker spectrometer with a 100 kHz field modulation, 1 G. Different microwave powers were used from 10 μ W to 10 mW. The microwave frequency has been determined using a Hewlett Packard 5352B frequency counter. All EPR spectra were recorded at 4 K and have been normalized to the gain and the sample mass.

Ti K-edge XANES spectra were measured at the LUCIA beamline (SLS, Switzerland), using Si(111) monochromators and a beam size of ~ 2 (H) \times 5 (V) μ m (K-B mirrors). The spectra were checked for energy calibration (± 0.1 eV) against fresnoite (5-coordinated Ti(IV)), anatase (6-coordinated Ti(IV)), Ti₂O₃ (6-coordinated Ti(III)) and metallic titanium foil. Although pre-edges are not a direct measure of the titanium coordination, the limited possibilities for the coordination in oxide glasses (namely tetrahedral, square pyramid, trigonal bipyramids and octahedral) makes the measurement of the pre-edge feature (position and intensity) a reliable measure of the average coordination of Ti in the probed material. Special care was given to obtain the best monochromator reliability (± 0.03 eV) by measuring the pre-edge for fresnoite model before and after each glass. Two scans were averaged to improve the signal to noise ratio.

RESULTS

Non-irradiated Glasses

The comparison of the Ti-K edge XANES spectra between DS1 and BS1 glasses (Fig. 1) shows significant differences in the pre-edge position suggesting a different average Ti(IV) environment and a same Ti redox. As a matter of fact, according to EPR analysis, trivalent titanium is absent in these glasses.

In order to analyze more precisely the Ti local environment, the normalized Ti pre-edge height was plotted as a function of the pre-edge position (Fig. 2) and compared to previous data taken from [4]. In disilicate glasses Ti (IV) is located in a mixture of five and six-coordinated sites (about 50/50) whereas

we estimate that in borosilicate glasses four-fold, five-fold and six-fold coordination coexist (about 15-35-55% respectively). This result is consistent with the presence of AlO₄ and BO₄ tetrahedra into the borosilicate glass structure consuming Na(I) cations for charge compensation. As a consequence, a lower Ti(IV) average coordination is required in BS compositions as compared to DS counterparts.

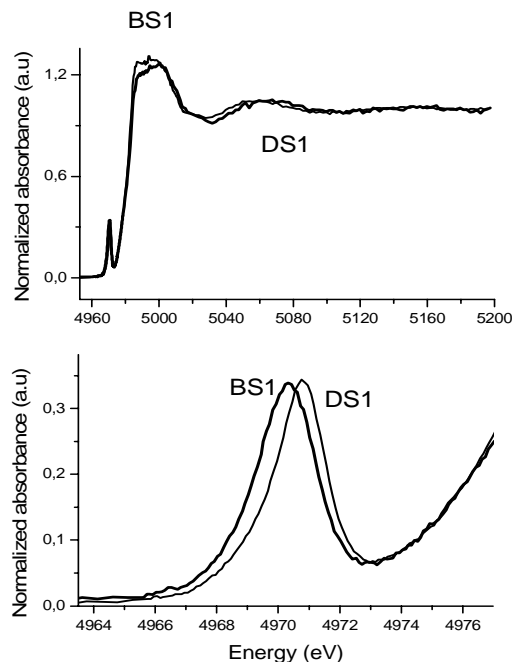


FIGURE 1. DS1 (straight line) and BS1 (bold line) Ti-K edge XANES spectra.

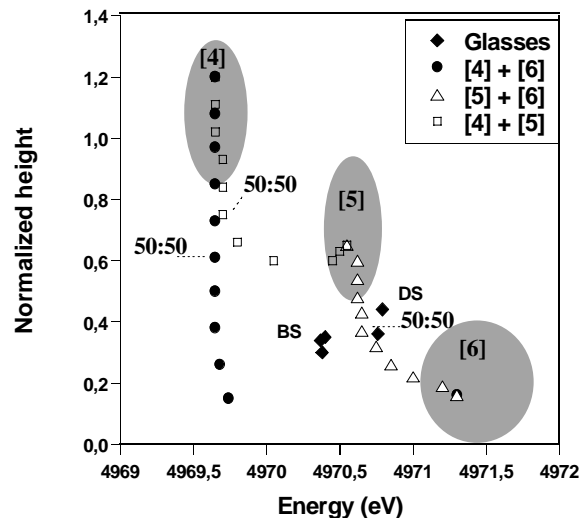


FIGURE 2. Normalized height vs energy of the Ti-pre-edge feature of non-irradiated glasses and comparison to data from [4].

Irradiated Glasses

Pre-edge Variation

The general variation of the irradiated glass pre-edge corresponds to an intensity decrease associated with a low-energy shift. For disilicate glasses, for the highest dose, the energy shift of the pre-edge feature is less important. The observed variation corresponds mainly to an intensity decrease of the pre-edge (Fig. 3).

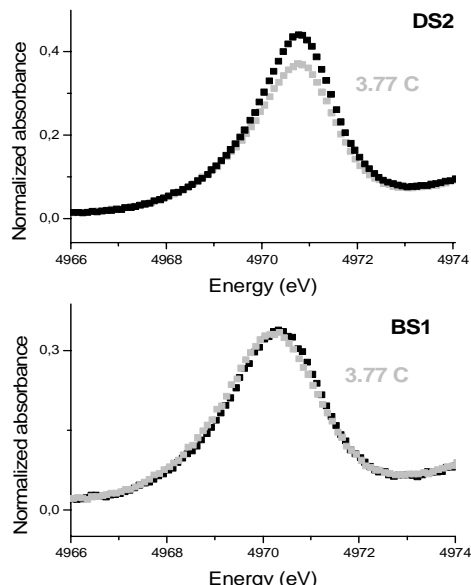


FIGURE 3. Irradiated (grey line) and non-irradiated (black line) Ti pre-edge of BS1 and DS2.

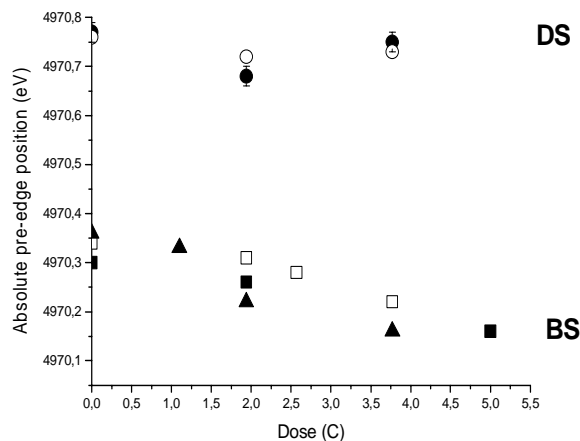


FIGURE 4. Pre-edge position of DS and BS glasses as a function of the irradiation dose (in Coulombs). Several compositions are displayed, non-irradiated glasses correspond to “0 C” dose.

The influence of the irradiation dose on the pre-edge position is represented in Fig. 4 for all compositions. A quasi linear shift of the pre-edge position as a function of the dose is displayed for all

borosilicate compositions contrary to the disilicate showing a minimum for 1.94 C. The effects on Ti pre-edge can be either due to a symmetry variation among the six-fold coordination of Ti(IV) under irradiation or to the presence of Ti(III) (or to both) as will be discussed below.

DISCUSSION

A careful and robust interpretation of the present XANES results needs a comparison with those obtained by EPR spectroscopy. This technique performed at 4K clearly demonstrates that Ti(III) amount increases with the irradiation dose for all borosilicate compositions. Moreover, for irradiation doses lower than 2 C, it is known that Na migration is rather low [2] so coordination change under irradiation can not occur easily, contrary to the case of higher doses (see for example the $\text{BO}_4 \rightarrow \text{BO}_3$ conversion [1]). Therefore, we can postulate that for the dose range [0-2C], the reduction of Ti(IV) is a predominant mechanism, as compared to Ti(IV) coordination change. This means that the increase in the Ti(III) amount under irradiation can be associated with an energy shift of the pre-edge in the BS series. The reduction of Ti(IV) without symmetry/coordination change would be the main mechanism to explain the observed changes in Ti K-edge XANES spectra for these glasses. However, the pre-edge position as a function of the dose does not show a linear variation in DS glasses (Fig. 4). For the highest dose (3.77C), the absence of significant energy shift of the pre-edge feature, associated to an intensity decrease (see Fig. 3) could thus be explained by the production of Ti(III) and a coordination change around Ti(IV). Further work is in progress to extract more quantitative understanding of the pre-edge feature of Ti(III) and its relations with Ti(IV).

ACKNOWLEDGMENTS

The authors would like to thank S. Guillous, T. Pouthier and V. Métayer for their help during the irradiation experiments.

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