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Ti³⁺ production under ionizing radiation in aluminoborosilicate glasses by EPR spectroscopy.

P. Lombard^{1*}, N. Ollier¹, B. Boizot¹

1. Laboratoire des Solides Irradiés, UMR 7642 CEA-CNRS-Ecole Polytechnique
Ecole Polytechnique, Route de Saclay, 91128 Palaiseau CEDEX, France

*Corresponding author: pierre.lombard@polytechnique.edu

Tél. : +33 (0) 1 69 33 45 02 – Fax. : +33 (0)1 69 33 46 54

Abstract: Reduction processes under irradiation of Ti⁴⁺ ions in aluminoborosilicate glasses have been studied by EPR spectroscopy at 20 K. Different parameters like the [Na]/[Ti] ratio and the integrated dose were analyzed in this work. Simulation of the Ti³⁺ ion EPR spectra has shown three different Ti³⁺ environment attributed to one ^[VI]Ti³⁺ and two ^[V]Ti³⁺ environment (square pyramid and trigonal bi-pyramid). The ^[VI]Ti³⁺ ion environment is observed only for higher [Na]/[Ti] ratios although the two others are observed for all values of the [Na]/[Ti] ratio considered.

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1. Introduction

Reduction processes under ionizing radiation has been observed in glasses for different ions like Sm³⁺ [1], Yb³⁺ [2] and Cr⁶⁺ [3]. In a recent work, we have studied by EPR spectroscopy combined with the simulation of Ti³⁺ EPR spectra the environment around Ti³⁺ ions produced under ionizing irradiation in silicate glasses [4]. We have shown that the Ti³⁺ EPR spectra is the sum of different components attributing to three different environments of Ti³⁺ ions denoted s_I , s_{II} and s_{III} . The relative proportions between the different Ti³⁺ sites depend mainly on the [Na]/[Ti] ratio and

therefore on the quantity of alkaline ions available for acting as charge compensator of Ti^{3+} ions with different coordination numbers. In silicate glasses, Ti^{4+} ions can be found under four main environments ($[VI]Ti^{4+}$, two $[V]Ti^{4+}$ and $[IV]Ti^{4+}$) [5]. We proposed to associate s_I and s_{III} sites with $[VI]Ti^{3+}$ ions and $[V]Ti^{3+}$ ions in a square pyramid geometry, respectively. The nature of the s_{II} site is still in discussion between a $[VI]Ti^{3+}$ with an oxygen vacancy and $[V]Ti^{3+}$ ions in trigonal bi-pyramid environments.

In the present study, our aim is to apply the method developed for silicate glasses to more complex Ti doped AluminoBoroSilicate (ABS) glass composition. By contrary of silicate glasses, a competition will exist between different ions (Al^{3+} , B^{3+} and Ti^{4+}) for trapping alkaline ions as charge compensators. This competition could limit the reduction efficiency of Ti^{4+} and therefore modify the nature of Ti^{3+} sites produced during ionizing radiation. According to the literature, G. El-Damrawi et al. [6] demonstrate by nuclear magnetic resonance spectroscopy that the Al^{3+} ions will consume first the alkaline ions. Then, the remaining Na^+ ions are used either by boron atoms to form B^{IV} species or non-bridging oxygen. In this work, we have also to take into account the titanium ions. However, to our knowledge, there is no study of the competition between titanium and others ions for consuming the Na^+ ions.

2. Experimental

The chemical compositions of our ABS glass samples are displayed in Table 1 and prepared by mixing appropriate amounts of analytical reagent grade in an agate mortar with ethanol. The powders were then transferred in a Pt-crucible and placed in an air-oven at $850^{\circ}C$ for 10 h to ensure a correct decarbonatation of different carbonate powders (Na_2CO_3). Then, the melt was heated to $1600^{\circ}C$ in 3h and

quenched. The obtained samples were cut and manually polished on a Labram HR Mecapol.

One important parameter indicated in Table 1 for ABS glasses is the $(\text{Na}/\text{Ti})^*$ ratio defined as following:

$$\left(\frac{\text{Na}}{\text{Ti}}\right)^* = \frac{2[\text{Na}_2\text{O}] - 2[\text{Al}_2\text{O}_3] - N_4[\text{B}_2\text{O}_3]}{[\text{TiO}_2]}$$

Where all the brackets denote the quantities of matter (in mol%) and N_4 is the ratio of B^{IV} to the total B_2O_3 amount. We assume for $(\text{Na}/\text{Ti})^*$ ratio that the titanium ions trap Na^+ ions after Al^{3+} and B^{3+} ions but before the production of non bridging oxygen. All samples were β -irradiated with electrons of 2.5 MeV (10 μA) and temperature lower than 80°C using a Van de Graaff accelerator (Laboratoire des Solides Irradiés, France). Different doses between 3.37×10^5 and 1.68×10^9 Gy were integrated.

X-band ($\nu = 9.490$ GHz) EPR spectra were recorded at 20 K using an OXFORD He cryostat with an EMX Bruker EPR spectrometer operating with a microwave power of 0.05 mW. The EPR spectra have been normalized to the receiver gain and to the sample weight. Simulation of Ti^{3+} EPR spectra were made using the ZFSFIT program developed by G. Morin and D. Bonnin [7]. The least square refinement process between simulated and experimental Ti^{3+} EPR spectrum gives access to the number and the nature of each Ti^{3+} sites in ABS glasses as a function of the integrated dose and glass compositions.

3. Results and discussion

Figure 1 presents the X-band EPR spectra of Ti^{3+} ions in β -irradiated ABS glasses with $(\text{Na}/\text{Ti})^*$ ratios between 5 and 115 and the spectrum of an undoped sample

(multiplied by factor 0.5 to improve lisibility). On this last one, the observed spectrum is attributed to defects produced during ionizing radiation. The nature of these defects has been previously studied by EPR spectroscopy in the non doped irradiated ABS glass composition [8]. On the spectra of the doped samples, we observe additional components of the spectrum, located between 3400 and 4000 Gauss and are attributed to Ti^{3+} ions. The spectrum of the defects is complex but it extends do not overlap the Ti^{3+} spectrum. Thus, hereafter will focus our study on the EPR spectrum of Ti^{3+} ions. Globally, Figure 1 clearly shows a dependence between the shape of the EPR spectrum and the $(Na/Ti)^*$ ratio. The EPR spectrum of the first sample, B5, is characterized by a positive peak around $g = 1.940 \pm 0.003$ with a shoulder at $g = 1.964 \pm 0.003$ and a negative peak at $g = 1.901 \pm 0.003$. When the $(Na/Ti)^*$ ratio increases to 40, the intensity of the positive peak at $g = 1.940 \pm 0.003$ increases relative to the intensity of the shoulder at $g = 1.901 \pm 0.003$. For higher $(Na/Ti)^*$ ratios, an additional EPR line characterized by $g_{\perp} = 1.973$ and $g_{\parallel} = 1.939$ is observed. We can attribute the evolutions of the EPR spectra to the presence of different Ti^{3+} EPR sites in the irradiated ABS glass EPR spectra. This Ti^{3+} ions site EPR spectrum appearing only at the higher $(Na/Ti)^*$ ratio was already observed in silicate glasses [4]. It was noted s_l and hereafter we will use the same denomination. By contrary, the other components of Ti^{3+} EPR spectra are different from those observed in our previous work with a $[Na]/[Ti]$ ratio less or equal to 40.

The figure 2 presents the evolution of the EPR spectra of two samples with the lowest (5) and the highest (115) $(Na/Ti)^*$ ratio as a function of the integrated dose. Before irradiation, no Ti^{3+} EPR lines are observed for all ABS glass compositions studied. At low $(Na/Ti)^*$ ratio (B5 sample) the intensity of the Ti^{3+} EPR spectrum increase with the dose without any significant EPR line shape changes. However at

high (Na/Ti)* ratio (B115 sample), the Ti^{3+} EPR spectrum of the sample irradiated at 3.37×10^5 Gy is characterized by one component with $g_{\perp} = 1.973$ and $g_{\parallel} = 1.945$ attributed to the s_I Ti^{3+} site. As a function of the integrated dose, additional Ti^{3+} EPR components defined by a positive peak at $g = 1.945$ and a broad negative peak at $g = 1.890$ are appearing. At higher dose, the relative intensity of the s_I EPR spectrum diminishes with respect to the other Ti^{3+} sites. This change in site proportions could be related to alkaline ions and oxygen migration under irradiation located in charge compensator position of titanium ions [9-12]. The decrease of s_I is showing therefore a decrease of the average coordination number around Ti^{4+} and/or Ti^{3+} ions at higher doses in ABS glasses.

The simulation of Ti^{3+} EPR spectra in irradiated Ti doped ABS glasses as a function of (Na/Ti)* and dose has been performed considering first that the s_I EPR spectrum is the same for both silicate and ABS glasses. The second point is that, due to the similarities between the Ti^{3+} EPR spectra in silicate and ABS glasses, we used the EPR parameters of the sites identified previously (s_{II} and s_{III}) as a starting point to refine the EPR parameters of the other Ti^{3+} sites in ABS glasses. Two other Ti^{3+} sites (b_{II} and b_{III}) were determined in irradiated ABS glasses with parameters given in Table 2. If we consider possible EPR lines broadening with the integrated dose due to dipole-dipole interactions, a linear combination of these three Ti^{3+} ion sites (s_I , b_{II} and b_{III}) allows us to reproduce the EPR spectra of all irradiated samples of this work. An example of simulation is presented in figure 3 for the B115 sample irradiated at 1.68×10^9 Gy. The first result associated to this work is that the s_I site is encountered in both silicate and ABS glass compositions showing therefore the lack of influence of other network formers (B^{3+} , Al^{3+}) on s_I EPR parameters. According to literature [13, 14], the s_I site EPR parameters reveal an octahedral environment around Ti^{3+} ions.

By contrary, the presence of boron and aluminum ions in network formers position influences the EPR parameters of s_{II} and s_{III} sites leading to b_{II} and b_{III} , respectively. These results could therefore show a specific speciation for these Ti^{3+} environments close to Al^{3+} and/or B^{3+} ions.

4. Conclusion

We have studied in this work by EPR the environment of Ti^{3+} ions produced under ionizing radiation in Ti-doped ABS glasses. We conclude to the existence of three different Ti^{3+} EPR sites, denoted s_I , b_{II} and b_{III} . The first one, s_I , is associated to a $[VI]Ti^{3+}$ in an octahedral environment and is observed only for the higher $(Na/Ti)^*$ ratio and integrated dose less than 1×10^9 Gy. The two other Ti^{3+} sites b_{II} and b_{III} , observed for all $(Na/Ti)^*$ ratios, could correspond to Ti^{3+} ions in fivefold environment by analogy with silicate glasses.

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Figure captions

Figure 1: EPR spectra of β -irradiated at $3 \cdot 10^7$ Gy ABS Glasses with $(\text{Na/Ti})^*$ of 0, 5, 40, 86 and 115.

Figure 2: Influence of the integrated dose between $3 \cdot 10^5$ and $1.68 \cdot 10^9$ Gy EPR spectra on the EPR spectra of B5 and B115 ABS glass samples.

Figure 3: Simulated and experimental EPR spectra of B115 sample irradiated at $3 \cdot 10^7$ Gy. The simulated EPR spectra of s_I , b_{II} and b_{III} are also presented in this figure

Tables

Sample	[SiO ₂]	[Na ₂ O]	[Al ₂ O ₃]	[B ₂ O ₃]	[TiO ₂]	(Na/Ti)*
B5	64.4	13.5	4.1	17.0	1	5
B40	55.2	25.8	3.5	14.6	0.9	40
B86	46.4	37.6	3.0	12.3	0.7	86
B115	42.2	43.3	2.7	11.2	0.6	115

Table 1: Ti doped ABS glass sample compositions. All quantities are in mol%.

See text for the definition of the (Na/Ti)*.

Site	g_x	g_y	g_z
s_I	1.939	1.970	
b_{II}	1.890	1.919	1.969
b_{III}	1.848	1.896	1.939
s_{II}	1.868	1.904	1.965
s_{III}	1.763	1.863	1.936

Table 2: EPR parameters of Ti³⁺ sites observed in β -irradiated ABS glasses. The EPR parameters of s_{II} and s_{III} Ti³⁺ sites in silicate glasses extracted from [Lombard et al., 2010] are also presented in table 2.

Figure 1

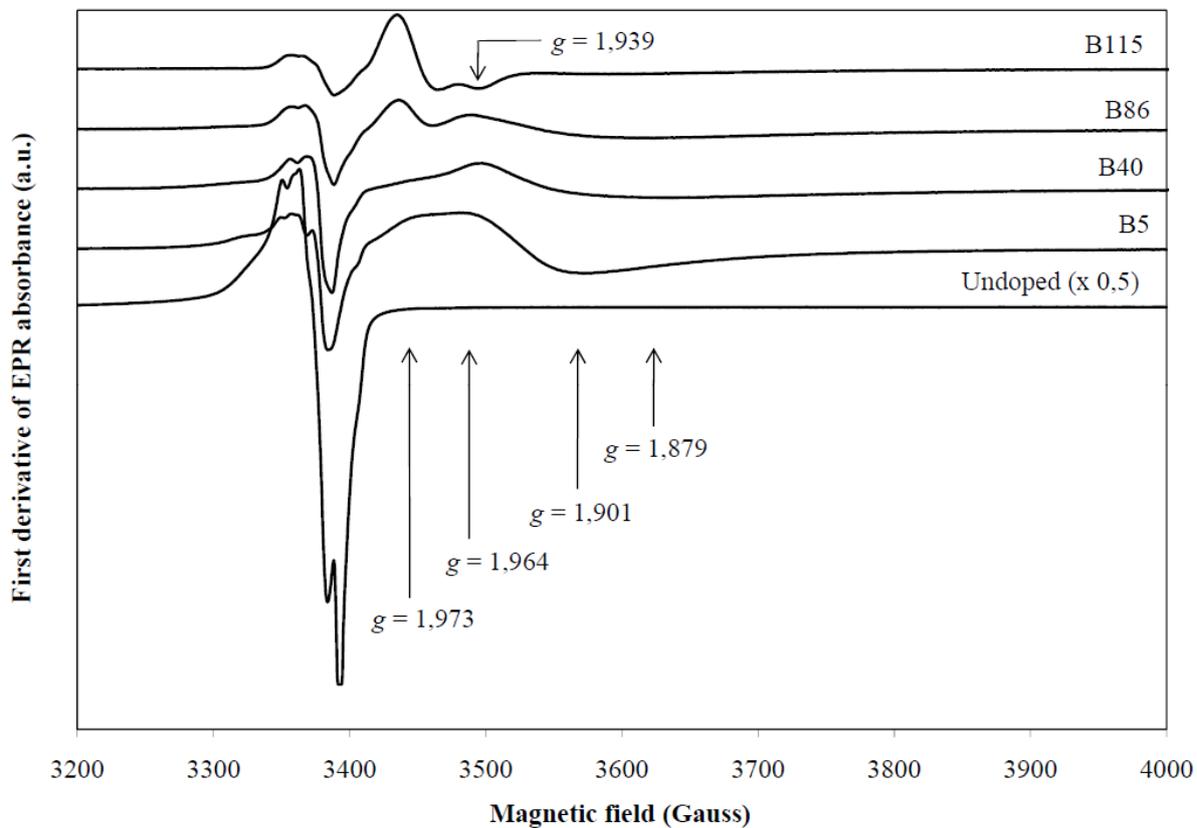


Figure 2

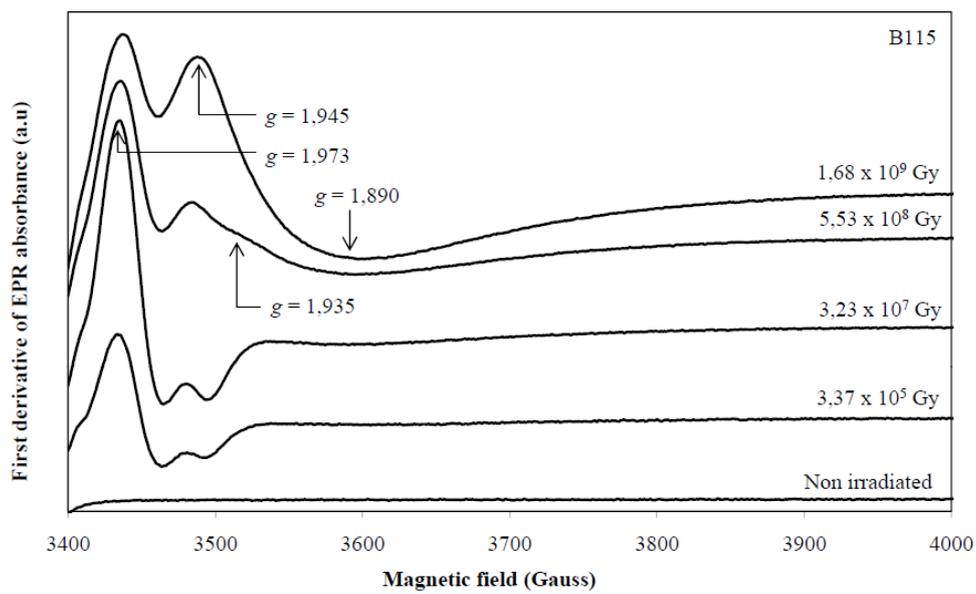
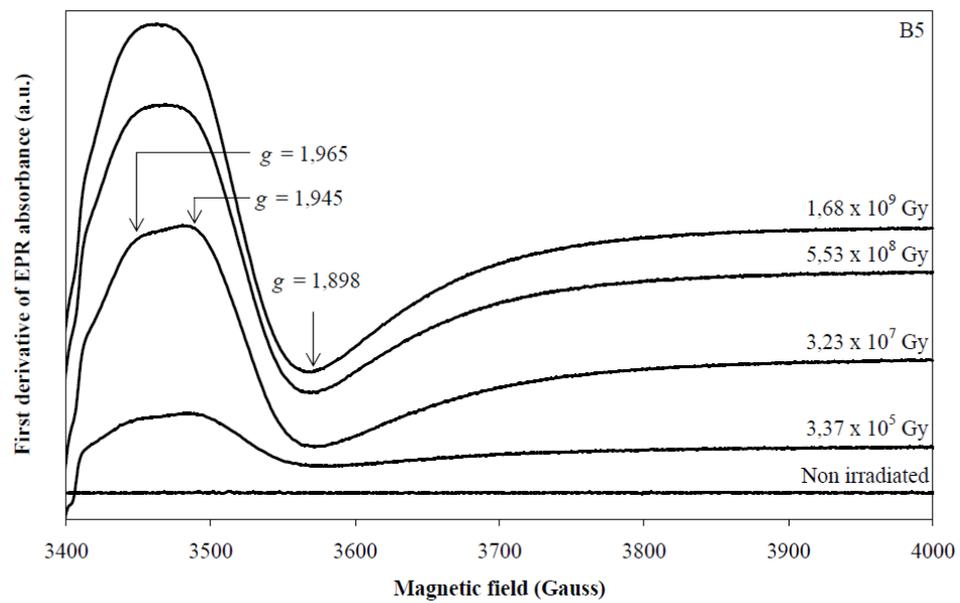


Figure 3

