

# $\beta$ -irradiation effect in aluminoborosilicate glasses: the role of RE-codoping (RE = Sm, Gd)

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Sm-, Gd-codoping effect on the structural modifications of  $\beta$ -irradiated aluminoborosilicate glasses has been studied by electron paramagnetic resonance (EPR) and Raman spectroscopy. The EPR spectra showed that the relative amount of  $Gd^{3+}$  ions occupying network former positions ( $Gd_{[n.f.]}^{3+}$ ) follows a non-linear behaviour as a function of the Sm/Gd ratio. This suggests that codoping favors occupation by  $Gd^{3+}$  ions of the network former rather than modifier positions in aluminoborosilicate glasses. We have observed the appearance of a superhyperfine structure of EPR lines attributed to boron oxygen hole centers (BOHC) with increasing Sm/Gd ratio. This suggests that  $Gd^{3+}$  ions are diluted in the vicinity of the BOHC defects. The concentration of the defects created by irradiation reveals a non-linear dependence on Sm, Gd-codoping for the lowest irradiation dose ( $10^5$  Gy). Therefore, codoping also affects the defect creation processes at least at the lowest irradiation dose. Raman spectroscopy measurements suggest that the irradiation-induced structural changes depend in a non-linear way on the Sm/Gd ratio. In fact, the shift of the Si–O–Si bending vibration modes reveals a clear minimum for the samples containing equal amounts of Sm and Gd (1:1) in the investigated glasses.

PACS: 61.43.Fs, 76.30.-v, 78.30.Ly

## 1. Introduction

Irradiation effects on glasses have been studied for a long time, especially in regard to high-level nuclear wastes glass disposal. This makes prediction of the long-term behaviour of this glass an essential aspect. For this purpose, simplified borosilicate glasses doped with rare-earth (RE) ions as models of the actinides are irradiated with electrons to simulate the consequences of  $\beta$  decay [1].

Our previous studies of single RE-doped aluminoborosilicate glasses showed that ionizing radiation gives rise to  $RE^{3+}$  reduction and modifications in the glass structure [2–4]. This has motivated our emphasis on the investigation of the interplay between structural evolution and reduction in aluminoborosilicate glasses subjected to irradiation in the hope of revealing a general trend in the behaviour of single RE-doped glasses. To the best of our knowledge, the effect of codoping as a process and of codopant concentrations on structural modifications in glass matrices has not been investigated.

We are going to present here the results of an analysis of the codoping effect on the ensuing changes in the glass structure, RE environment and the RE reduction process. Codoping appears to be a convenient way for observation of the changes occurring both in the glass structure and in the charge state of RE ions.

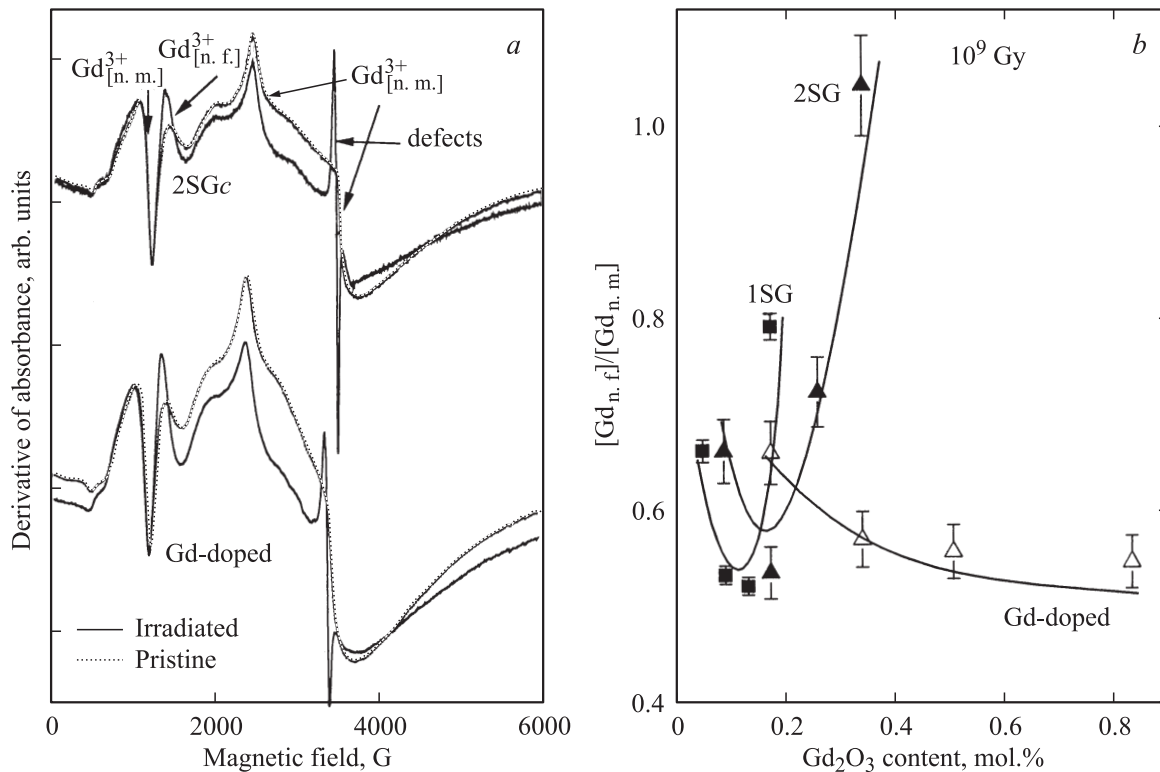
## 2. Experimental

Two glass materials were fabricated with the total concentrations of the  $Sm_2O_3$  and  $Gd_2O_3$  mixture of 0.17 (1SG) and 0.34 (2SG) mol.% of the total RE oxide mass. Sm-, Gd-doped borosilicate glasses were prepared by adding to the 5 oxide borosilicate glass base different amount of rare earth oxides taken in proportions Sm/Gd 1:3 (SGa), 1:1 (SGb) and 3:1 (SGc). The 5-oxide base glass has

the following composition: 59.77%  $SiO_2$ , 3.84%  $Al_2O_3$ , 22.41%  $H_3BO_3$ , 12.12%  $Na_2CO_3$ , and 1.7%  $ZrO_2$  (in mol.%). The glass synthesis and the techniques employed are presented elsewhere [2–4]. All samples were irradiated with 2.5 MeV electrons generated by a Van de Graaf accelerator. The glass thickness was about 0.5 mm in order to reach uniform irradiation in the glass volume. The EPR spectra were obtained with an X band ( $\nu \approx 9.420$  GHz) EMX Bruker spectrometer at room temperature with a 100 kHz field modulation, 1 G amplitude modulation and 1 mW microwave power. All EPR spectra have been normalized against a sample weight of 100 mg. The Raman spectra were measured after irradiation on a Labram HR micro-spectrometer using the 514.5 nm line of an  $Ar^+$  laser.

## 3. EPR spectra

Fig. 1, *a* presents the EPR spectra of a pristine and a heavily irradiated codoped glass. According to Ref. [2,5] the EPR signal at  $g \sim 2.0, 2.8, 6.0$  and  $g \sim 4.8$  is produced by  $Gd^{3+}$  ions located in the network modifier ( $Gd_{[n.m.]}^{3+}$ ) and network former ( $Gd_{[n.f.]}^{3+}$ ) positions, respectively (Fig. 1, *a*). Exposure to  $\beta$ -irradiation at doses about  $10^9$  Gy leads to the appearance of an additional defect line around  $g \sim 2.0$ , and it derives from Gd ions occupying the network former sites. We investigated the correlation between the intensities of the EPR lines attributed to the  $Gd_{[n.m.]}^{3+}$  and  $Gd_{[n.f.]}^{3+}$  sites before and after the irradiation for both series of the Sm-, Gd-codoped aluminoborosilicate glasses (1SG and 2SG); the corresponding graphs are plotted in Fig. 1, *b* vs. the Sm/Gd molar ratio. The obtained ratio between  $Gd_{[n.f.]}^{3+}$  and  $Gd_{[n.m.]}^{3+}$  sites follows a non-linear behaviour, with the Sm/Gd ratio exhibiting a distinct minimum for samples codoping equally (1:1). By contrast, in single Gd-doped glasses, the number of  $Gd^{3+}$  ions occupying network former positions



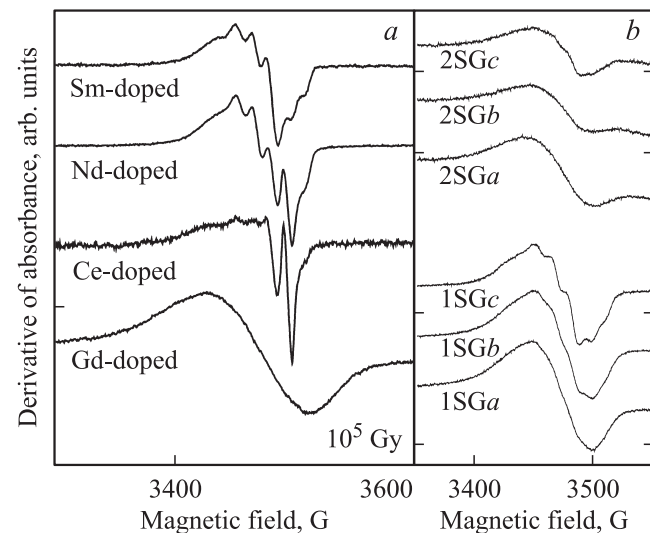
**Figure 1.** EPR spectra of 0.34 mol.% codoped (amount of rare earth oxide in proportion Sm/Gd 3:1 (2SGc)) and Gd-doped aluminoborosilicate glasses (a); relative amount of  $Gd^{3+}$  ions located in network former positions as a function of  $Gd_2O_3$  concentration for codoped and single doped glasses (b). The line is a guide for the eyes only.

is minimized by the gadolinium oxide concentration in a monotonic manner as shown in Fig. 1, b. Codoping, therefore, favors preferable location of  $Gd^{3+}$  ions in network former rather in modifier positions.

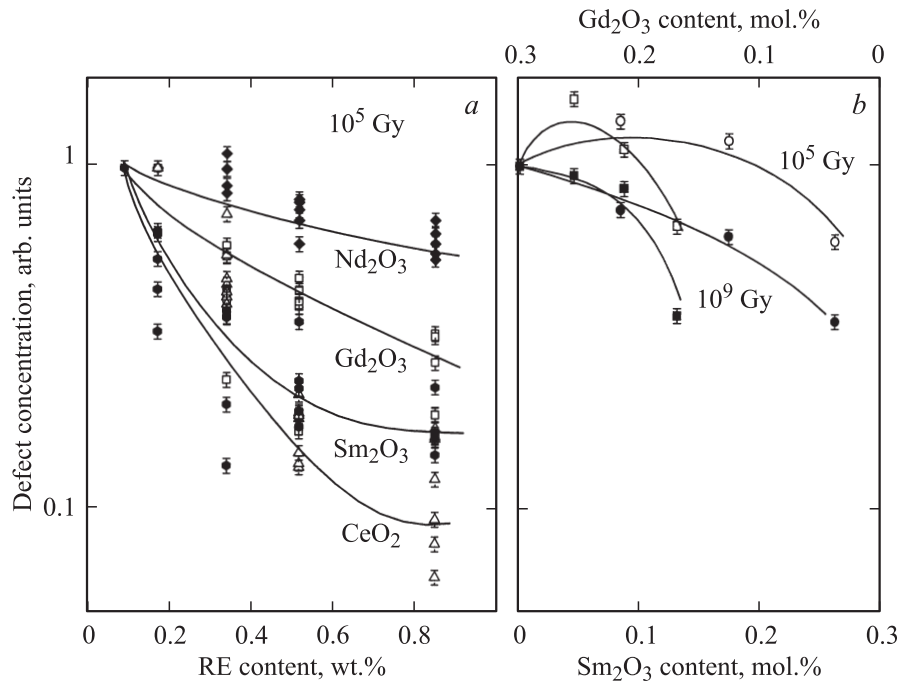
Fig. 2, a displays EPR spectra of aluminoborosilicate glasses doped with different RE elements and irradiated with  $10^5$  Gy. A part of the high field region is shown on a finer scale. It is known that the EPR spectrum of irradiated glasses is complex and is actually the sum of EPR lines from several paramagnetic centers, although its major component derives from the boron oxygen hole center (BOHC) ( $\equiv B-O^{\bullet}$ ) resonance [6]. We can observe in the Fig. 2, a a weak evolution of the EPR line as a function of the glass chemical composition (for different RE-dopants). Similar EPR resonances are encountered in all EPR spectra. In particular, incorporation of Sm, Nd and Ce ions induces only variations of the shape and intensity of the irradiated glass EPR spectrum. At the same time, the EPR resonance of the Gd-doped glass reveals no sign at all of a resolved structure. The 1SG and 2SG glass EPR spectra plotted vs. the Sm, Gd-codoping ratio exhibit some differences (Fig. 2, b). It is seen that an increase of the Sm/Gd ratio leads to the appearance of superhyperfine structure of BOHC defects. This structure of the defect line is most noticeable at low  $Sm_2O_3$  contents in codoped 1SG samples (sample 1SGb). However, the ability to discern the structure of the defects diminishes with the increase of the total RE content from 0.17 (1SG) to 0.34 (2SG) mol.% and

resolution can be obtained only for the samples with Sm/Gd ratio above 3/1 (2SGc) (Fig. 2, b).

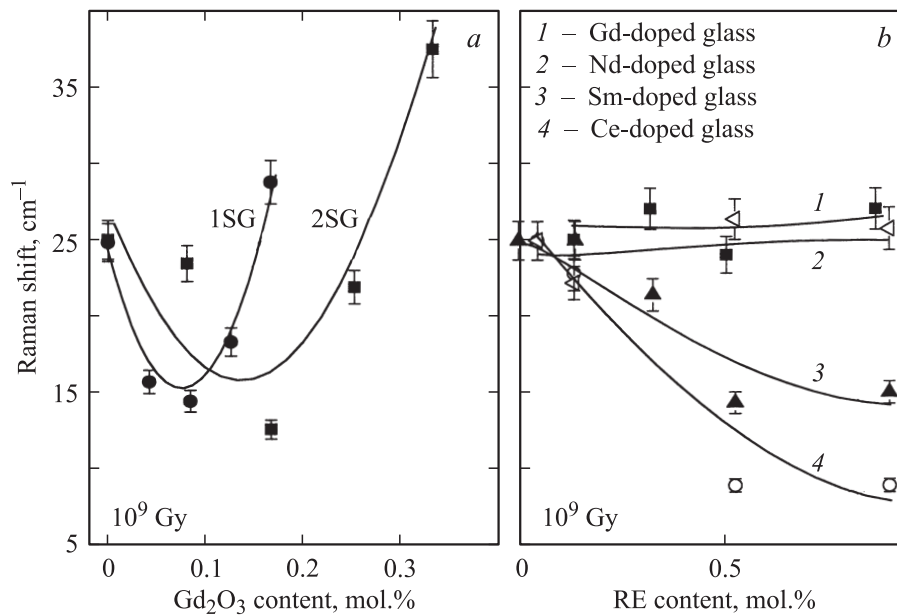
EPR spectroscopy offers a possibility of estimating the concentration of paramagnetic defects. We estimated the influence of RE concentration on the amount of defects



**Figure 2.** Changes in the EPR spectra of different RE-doped (a) and Sm-, Gd-codoped aluminoborosilicate glasses (defect region at  $g \sim 2$ ) plotted vs. Sm content for different Sm/Gd proportions — 1:3 (SGa), 1:1 (SGb) and 3:1 (SGc) (b).



**Figure 3.** Defect concentration as a function of different RE for all irradiation doses (a) and of Sm content for 10<sup>5</sup> and 10<sup>9</sup> Gy (b). The line is a guide for the eyes only.



**Figure 4.** Raman shift of Si-O-Si bending vibration modes for Sm-, Gd-codoped aluminoborosilicate glasses plotted as a function of Gd content (a) and different RE-doped aluminoborosilicate glasses plotted vs. RE content (b). The line is the guide for the eyes only.

produced by irradiation. Fig. 3,*a* shows that for all single RE-doped glasses, an increase of the dopant concentration brings about a decrease of the number of defects. On the contrary, the defect concentration in codoped glasses follows a non-linear dependence on the Sm/Gd ratio (Fig. 3,*b*) at the lowest irradiation fluence. Therefore, codoping can strongly affect also the defect creation processes, at least at the lowest irradiation doses.

#### 4. Raman spectra

Raman studies of aluminoborosilicate glasses have shown that for at the highest irradiation doses (10<sup>9</sup> Gy), a progressive longward shift is observed of the 460 cm<sup>-1</sup>, vibration band, which corresponds to a decrease of the average Si-O-Si bond angle as well as a decrease of the average ring size [7]. This is typical for these glasses, both without

dopants and single RE-doped, and it was reported in [2,5,8]. Nevertheless, non-linear evolution of the Si-O-Si bending vibration modes shift is apparently revealed with an increase of the relative fraction of gadolinium oxide (Fig. 4, *a*). Moreover, this relation dependence showed a completely different behavior compared with Raman shift of the same Si-O-Si modes in other single-doped aluminoborosilicate glasses, as it is shown in Fig. 4, *b*.

## 5. Discussion

In order to predict the long-term behaviour of realistic nuclear waste glasses, simplified borosilicate glasses doped with some RE elements to simulate the actinides were irradiated with electrons to model the effects of  $\beta$ -decay [1]. Recently we have shown that structural modifications in aluminoborosilicate glasses doped with rare-earth ions under irradiation are correlated with the content and nature of the RE-dopant [2–4]. According to [2–4], the weakening of some structural changes induced by ionizing radiation, more specifically, sodium migration, Raman shift of the Si-O-Si bending vibration mode and point defect creation can be linked to the relative stability of the different redox states of the RE ion. As follows from the results presented, double-doped and single-doped aluminoborosilicate glasses containing Sm, Ce and/or Gd, Nd reveal completely different behavior under irradiation, a feature evidenced both by the EPR and Raman spectroscopy. Taking into consideration the ability of some RE elements to be reduced, and also the influence of this process on both the structural evolution and defect creation, it could be suggested that mixing of these two dopants in the glasses under study should exhibit a monotonic dependence of structural changes and defect creation on RE content in the mixed series from Gd to Sm, related with the increase of the Sm/Gd ratio. In fact, as it can be seen from the Fig. 1, *b*, for each glass series (1SG and 2SG) the  $Gd_{n.f.}/Gd_{n.m}$  ratio follows a non-linear dependence on Gd content. However, with no mixing this relation reveals a distinct monotonic falloff (Fig. 1, *b*). It should apparently be ascribed to some mixed RE effect.

The shape of the EPR line originating from defects in different RE-doped glasses presented in Fig. 2, *a* reveals some variations. The nature of the defects is thoroughly considered in Ref. [6]. We can infer from this result that only a fraction of the defects becomes modified. At the same time the unresolved structure of the EPR defect line of Gd-doped glass suggests that in the case of Gd incorporation in aluminoborosilicate glass matrix the RE ions are located in the vicinity of the BOHC defects created by irradiation. Evidence for a specific distribution of  $Gd^{3+}$  ions in borosilicate glasses was already suggested by Raman spectroscopy measurements which were performed on borosilicate glasses doped with the highest  $Gd_2O_3$  content [8]. Therefore, it appears reasonable to assume that the specific broadening of the line shape is due to dipole-dipole interaction between the gadolinium ions and defects. The evolution in structure of the EPR defect line

is also observed for both series of codoped glasses with different fractions of Sm, Gd, up to single-doped samples (Fig. 2, *b*). The modifications are therefore induced by the incorporation of Gd ions. It should be noted that variations of defect concentration produced during irradiation at a fluence of  $10^5$  Gy in mixed Sm-, Gd-doped glasses depends on the RE mixing, and that this effect has a tendency to decrease with increasing fluence (Fig. 3, *b*). One explanation could be that the environment of both Gd and Sm ions (coordination number and redox state) changes also as a function of the dose and, therefore, it could exert an influence on the processes involved in defect production.

The phenomenon of a non-linear change of some glass physical properties with the ratio of two alkali ions present is referred to in the literature as the „mixed alkali effect“ (MAE) [9]. It was suggested that MAE leads to suppression of alkali migration and to blocking of structural modifications under irradiation [9]. Unlike MAE, RE mixing does not preclude structural changes. As shown in Fig. 4, *a*, the shift of the Si–O–Si bending vibration modes correlating with the non-linear dependence on defects concentration reveals clearly a non-linear character of the behavior with Sm/Gd ratio (Fig. 3, *b*). By contrast, for single doped glasses the shift of this band seems to be linked to the ability of RE ions to reduce and to the amount of defects produced during ionizing irradiation (Fig. 4, *b*). In fact, in Nd- or Gd-doped glasses where reduction is negligible, an increase in the Nd- or Gd-doping level leads to a moderate decrease of the amount of defects with increasing Nd or Gd content. At the same time, an increase in the Nd or Gd concentration does not influence the structural modifications revealed by Raman spectroscopy (Fig. 4, *b*). On the other hand, as it can be seen from Fig. 4, *b*, the presence of reduction, similar to the case of Ce- or Sm-doping, has a tendency to some blocking of the structural modifications, and the amount of defect decreases promptly (Fig. 3, *a*). Therefore, taking into account this consideration, the impact of RE mixing should reveal a linear dependence of both the amount of defects and of structural changes as a function of RE content, as one progresses along the series from the single Gd to the single Sm doping case. But, in view of the observed correlation between non-linear patterns of both the structural evolution and defect creation, it may be supposed that there exist some additional types of processes connected probably with interaction among the RE ions. Moreover, taking into account that the contributions of the processes involved in the absorption of ionizing radiation by codoped glasses may be different [10], and also that RE ions can interact with one another in more than one way [11], it becomes obvious that the interpretation of the RE mixed effect is not straightforward and requests for its solution further investigation by the luminescence techniques.

## 6. Conclusion

Our study has shown that the observed irradiation-induced structural evolution in both investigated series of aluminoborosilicate glasses (1SG and 2SG) is due to the

RE mixed effect. The non-linear dependence of the  $Gd^{3+}$  ion content residing in the network former sites and of structural modifications, namely, the Raman shift of the Si–O–Si bending vibration modes induced by  $\beta$ -irradiation with increasing Sm/Gd ratio results from the RE-codoping. The present work is a continuation of an investigation aimed at a search for general interrelations mediating structural changes and the reduction mechanism in rare-earth doped aluminoborosilicate glasses exposed to ionizing radiation.

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