b-Irradiation Effect in Aluminoborosilicate Glasses: The Role of RE Codoping (RE= Sm, Gd)

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ABSTRACT

The effect of Sm and Gd codoping on the structural modifications of β-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 ( ) follows a nonlinear behavior as a function of the Sm/Gd ratio. This suggests that codoping favors the occupation by Gd^{3+} ions of the network former positions rather than the modifier positions in aluminoborosilicate glasses. The appearance of a superhyperfine structure of EPR lines attributed to boron–oxygen hole centers (BOHC) with increasing Sm/Gd ratio was observed. This suggests that Gd^{3+} ions are diluted in the vicinity of the BOHC defects. The concentration of defects created by irradiation reveals a nonlinear dependence on Sm and 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 vary nonlinearly with the Sm/Gd ratio. In fact, the shift of the Si–O–Si bending vibration modes reveals a clear minimum for samples containing equal amounts of Sm and Gd (1 : 1) in the investigated glasses.

1. INTRODUCTION

Irradiation effects on glasses have been studied for a long time, especially in regard to high-level nuclearwaste glass disposal. This makes prediction of the long term behavior of such glasses 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 β decay [1]. Our previous studies of singly *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 behavior of singly *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 present here the results of analyzing 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 total concentrations of a Sm_2O_3 and Gd_2O_3 mixture of 0.17 (1SG) and 0.34 (2SG) mol % of the total *RE* oxide mass. Sm- and Gd-doped borosilicate glasses were prepared by adding to the 5-oxide borosilicate glass base different amounts of rare-earth oxides taken in the following Sm/Gd proportions: 1 : 3 (SG*a*), 1 : 1 (SG*b*), and 3 : 1 (SG*c*). 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 mole percent). 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 Graaff 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 are 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

Figure 1a presents the EPR spectra of a pristine and a heavily irradiated codoped glass. According to [2, 5], the EPR signal at $g\sim$ 2.0, 2.8, and 6.0 and $g\sim$ 4.8 is produced by Gd^{3+} ions located in the network modifier ($Gd^{3+}_{[nm]}$) and network former ($Gd^{3+}_{[nf]}$) positions, respectively

(Fig. 1a). Exposure to β irradiation at doses of about 10^9 Gy leads to the appearance of an additional defect line around $g \sim 2.0$, which derives from Gd ions occupying the network former sites. We investigated the correlation between the intensities of the EPR lines attributed to the $Gd^{3+}_{[nm]}$ and $Gd^{3+}_{[nf]}$ sites before and after the irradiation for both series of Sm and Gd-codoped aluminoborosilicate glasses (1SG and 2SG). The corresponding graphs are plotted vs. Sm/Gd molar ratio in Fig. 1b. The obtained ratio between the $Gd^{3+}_{[nf]}$ and $Gd^{3+}_{[nm]}$ sites varies nonlinearly with the Sm/Gd ratio, exhibiting a distinct minimum for equally codoped (1 : 1) samples. By contrast, in singly Gddoped glasses, the number of Gd^{3+} ions occupying network former positions is minimized by the gadolinium oxide concentration in a monotonic manner as shown in Fig. 1b. Codoping, therefore, favors the location of Gd^{3+} ions in the network former positions rather than in the modifier positions. Figure 2a displays the EPR spectra of aluminoborosilicate glasses doped with various *RE* elements and irradiated to a dose of 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 a sum of EPR lines from several paramagnetic centers, although its major component derives from the boron–oxygen hole center (BOHC) (≡B–O$^\bullet$) resonance [6]. In Fig. 2a, we can observe a weak evolution of the EPR line as a function of the glass chemical composition (for different *RE* dopants). Similar EPR signals are encountered in all EPR spectra. In particular, the incorporation of Sm, Nd, and Ce ions induces only variations in the shape and intensity of the irradiated-glass EPR spectrum. However, the EPR signal of a Gd-doped glass reveals no sign of a resolved structure. The 1SG and 2SG glass EPR spectra plotted vs. the Sm/Gd codoping ratio exhibit some differences (Fig. 2b). It is seen that an increase in the Sm/Gd ratio leads to the appearance of a 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 1SG*b*). However, the ability to discern the structure of the defects diminishes as the total *RE* content increases from 0.17 (1SG) to 0.34 mol % (2SG) and resolution can be obtained only for the samples with Sm/Gd ratio above 3/1 (2SG*c*) (Fig. 2b). EPR spectroscopy offers a possibility of estimating the concentration of paramagnetic defects. We estimated the influence of the *RE* concentration on the amount of defects produced by irradiation. It can be seen in Fig. 3a that, for all singly *RE*-doped glasses, an increase of the dopant concentration brings about a decrease in the number of defects. On the contrary, the defect concentration in codoped glasses follows a nonlinear dependence on the Sm/Gd ratio (Fig. 3b) at the lowest irradiation fluence. Therefore,

codoping can also strongly affect the defect creation processes, at least at the lowest irradiation doses.

4. RAMAN SPECTRA

Raman studies of aluminoborosilicate glasses show that, at the highest irradiation dose (10^9 Gy), a progressive long ward shift of the 460 cm^{-1} vibration band is observed, 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 of these glasses, both without dopants and singly *RE*-doped, and it was reported in [2, 5, 8]. Nevertheless, nonlinear evolution of the shift of the Si–O–Si bending vibration modes is apparently revealed with an increase in the relative fraction of gadolinium oxide (Fig. 4a). Moreover, this dependence showed a completely different behavior as compared with the Raman shift of the same Si–O–Si modes in other singly doped aluminoborosilicate glasses, as shown in Fig. 4b.

5. DISCUSSION

In order to predict the long-term behavior of actual nuclear waste glasses, simplified borosilicate glasses doped with some *RE* elements to simulate the actinides were irradiated with electrons to model the effects of β 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, doubly and singly doped aluminoborosilicate glasses containing Sm, Ce, and/or Gd and Nd reveal completely different behavior under irradiation; a feature evidenced both by 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 the *RE* content in the mixed series from Gd to Sm,

related with the increase of the Sm/Gd ratio. In fact, as can be seen from Fig. 1b, for each glass series (1SG and 2SG), the Gdn.f/Gdn.m ratio follows a nonlinear dependence on Gd content. However, with no mixing, this relation reveals a distinct monotonic falloff (Fig. 1b). It should apparently be ascribed to some mixed *RE* effect. The shape of the EPR line originating from defects in the different *RE*-doped glasses presented in Fig. 2a reveals some variations. The nature of the defects is thoroughly considered in [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 a Gd-doped glass suggests that, in the case of Gd incorporation in an aluminoborosilicate glass matrix, the *RE* ions are located in the vicinity of the BOHC defects created by irradiation. Evidence for a specific distribution of Gd3+ ions in borosilicate glasses has already been provided by Raman spectroscopy measurements performed on borosilicate glasses doped with the highest Gd_2O 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 of the structure of the EPR defect line is also observed for both series of codoped glasses with different fractions of Sm and Gd, up to singly doped samples (Fig. 2b). The modifications are therefore induced by the incorporation of Gd ions. It should be noted that variations in defect concentration produced during irradiation at a fluence of 10^5 Gy in mixed Sm- and Gd-doped glasses depend on the *RE* mixing and that this effect has a tendency to decrease with increasing fluence (Fig. 3b). One explanation of this fact could be that the environment of both Gd and Sm ions (coordination number and redox state) also changes as a function of the dose and, therefore, it could exert an influence on the processes involved in defect production. The phenomenon of a nonlinear change in some physical properties of glasses 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. 4a, the shift of the Si–O–Si bending vibration modes correlating with the nonlinear dependence on defect concentration clearly reveals a nonlinear behavior with Sm/Gd ratio (Fig. 3b). By contrast, for singly doped glasses, the shift of this band seems to be linked to the ability of *RE* ions to reduce and is dependent on the amount of defects produced during ionizing irradiation (Fig. 4b). 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 in

the amount of defects with increasing Nd or Gd content. At the same time, anincrease in the Nd or Gd concentration does not influence the structural modifications revealed by Raman spectroscopy (Fig. 4b). On the other hand, it can be seen from Fig. 4b that the presence of reduction, as in the case of Ce- or Sm-doping, has a tendency towardsome blocking of the structural modifications, and the amount of defects decreases rapidly (Fig. 3a). Therefore, taking into account this fact, the impact of *RE* mixing should reveal a linear variation of the amount of defects and structural changes with the *RE* content along the series from the single Gd to the single Sm doping case. However, in view of the observed correlation between the nonlinear 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 from 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 requires for its solution further investigation by the luminescence techniques.

6. CONCLUSIONS

Our study has shown that the observed irradiationinduced structural evolution in both investigated series of aluminoborosilicate glasses (1SC and 2SG) is due to the rare-earth (*RE*) mixed effect. The nonlinear variation 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 β irradiation) with increasing Sm/Gd ratio results from the *RE* codoping. The present work is a continuation of an investigation aimed at searching for general interrelations mediating structural changes and the reduction mechanism in *RE*-doped aluminoborosilicate glasses exposed to ionizing radiation.

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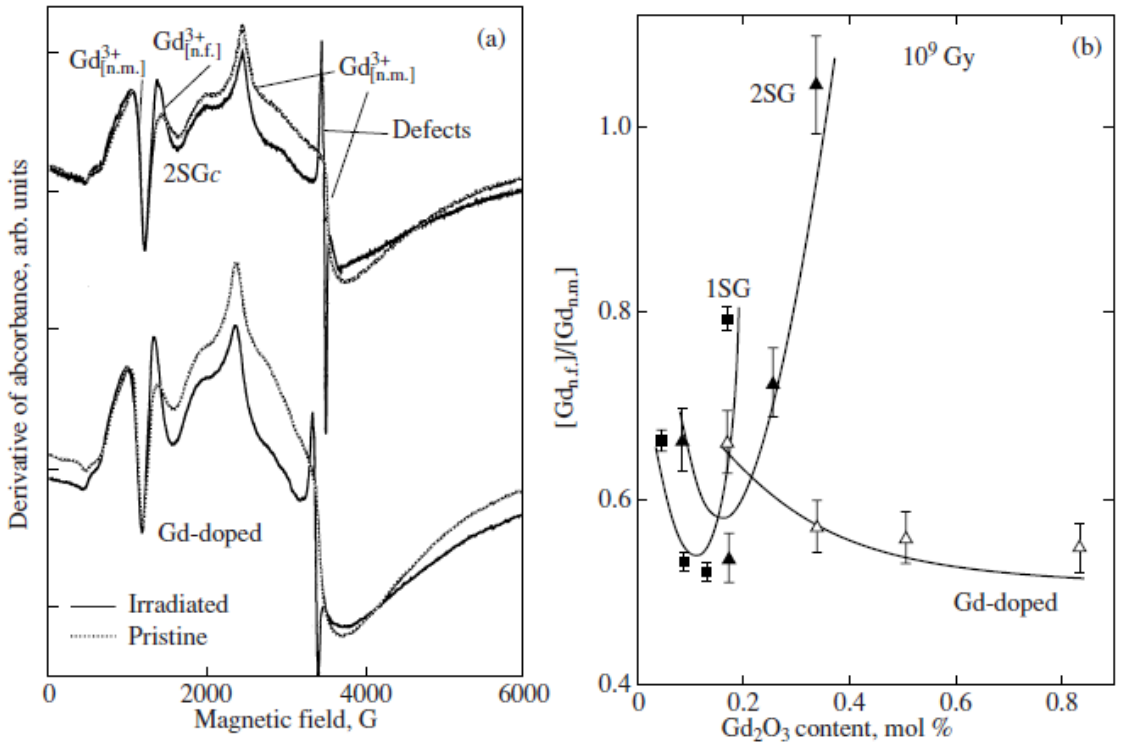

Fig. 1. (a) EPR spectra of 0.34 mol % codoped (*RE* oxide amounts with a Sm/Gd ratio of 3: 1 (2SG*c*)) and Gd-doped aluminoborosilicate glasses. (b) Relative amount of Gd^{3+} ions located in network former positions as a function of Gd_2O_3 concentration for codoped and singly doped glasses (the lines are guide to the eye only).

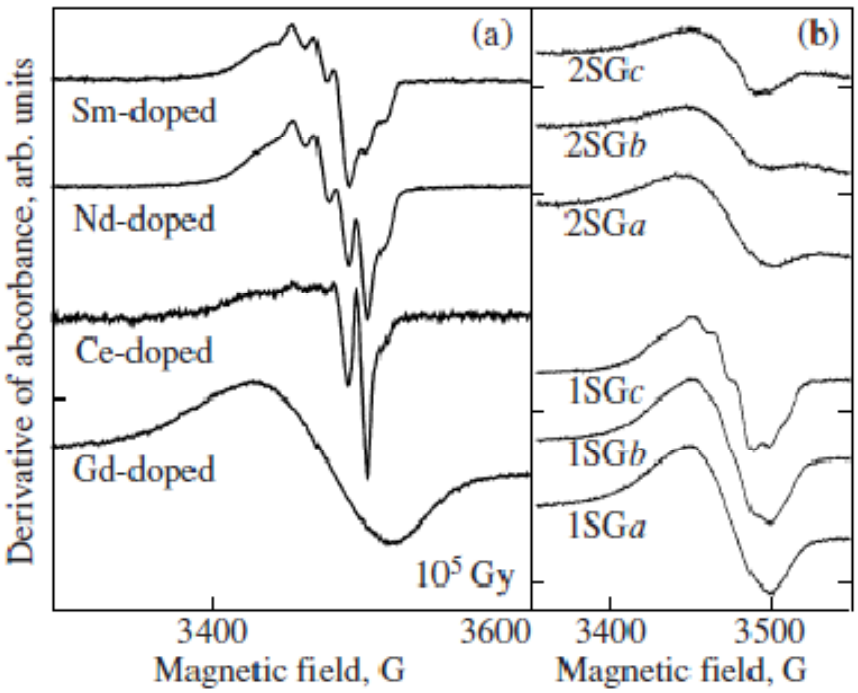

Fig. 2. Changes in the EPR spectra of various (a) *RE*-doped and (b) Sm- and Gd-codoped aluminoborosilicate glasses (defect region at $g \sim 2$) plotted vs. Sm content for the following values of the Sm/Gd ratio: 1 : 3 (SG*a*), 1 : 1 (SG*b*), and 3 : 1 (SG*c*).

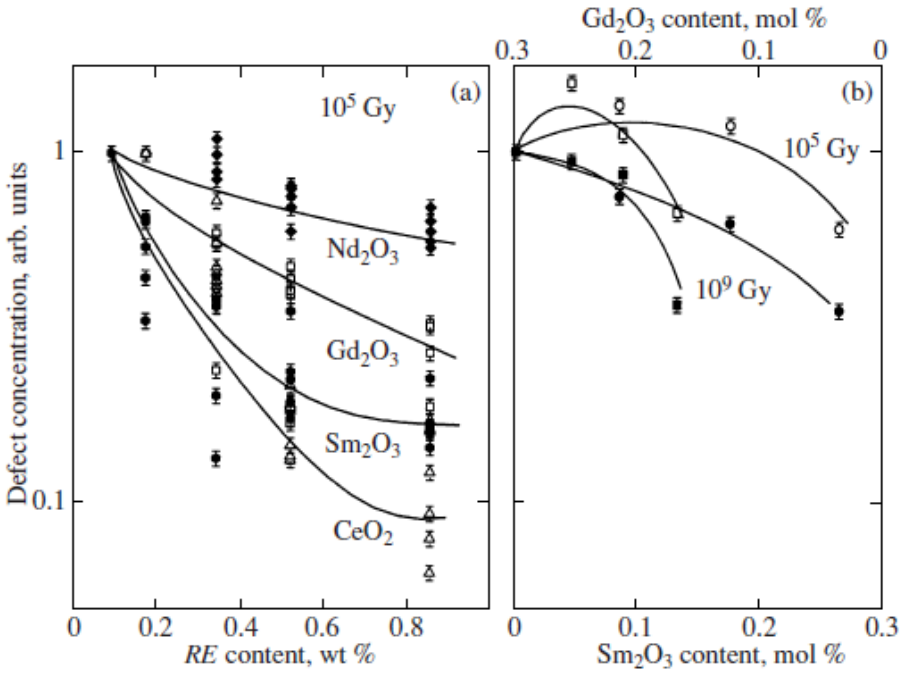

Fig. 3. Defect concentration as a function (a) of the content of different *RE* for all irradiation doses and (b) of Sm content for doses of 10^5 and 10^9 Gy. The lines are guide for the eye only.

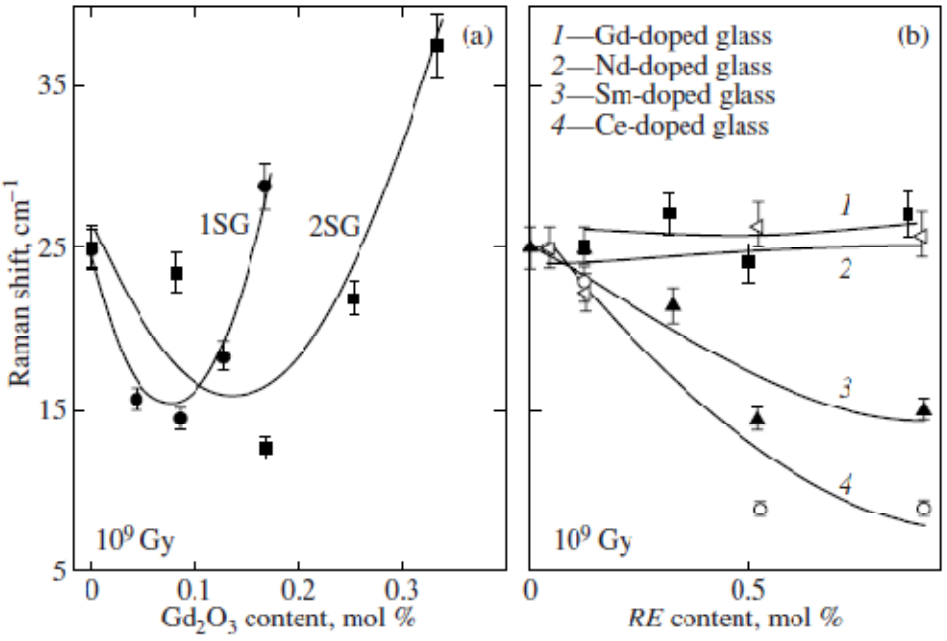

Fig. 4. Raman shift of the Si–O–Si bending vibration modes for (a) Sm- and Gd-codoped aluminoborosilicate glasses plotted as a function of Gd content and (b) various *RE*-doped aluminoborosilicate glasses plotted vs. *RE* content. The lines are guide for the eye only.