Optical properties and valence state of Sm ions in aluminoborosilicate glass under β-irradiation

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Abstract

Sm-doped borosilicate glasses exposed to β-irradiation with doses from 8 × 10⁵ up to 4 × 10⁹ Gy have been studied by luminescence, Raman and electron paramagnetic resonance (EPR) spectroscopies. The luminescence spectra for pristine and irradiated glasses reveal that the β-irradiation process affects valence state of samarium ions. Intense emission at 684 and 727 nm excited by Ar⁺ laser (514.5 nm) due to the transition of Sm ²⁺ ion was observed after irradiation. Relative proportion of Sm ²⁺ ions estimated as a function of both Sm₂O₃ content and irradiation dose has the tendency to increase with increasing irradiation dose. In contrast, the EPR spectra of the studied samples reveal a decrease of the defect content, which are mostly hole defects, produced during irradiation, as a function of Sm₂O₃ content. Finally, the addition of Sm₂O₃ leads to a decrease of the Si–O–Si bending vibration modes shift and polymerisation changes under irradiation.

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1. Introduction

Glasses doped with rare-earth (RE) atoms are well-known as fluorescent substances because of their high-luminescence efficiency. Glasses containing various RE ions are seen as promising materials for quantum electronics devices such as high power lasers [1–3]. Sm²⁺-doped glasses are quite attractive since spectral hole burning observed in various matrices containing Sm³⁺ ions showed relatively high thermal stability [4–7]. Because of its potential use in optical data-storage in high-density memory devices, there have been extensive investigations on the optical properties of Sm²⁺-doped glasses [8–10].

The reduction mechanism of Sm³⁺ ions into Sm²⁺ has been observed in aluminosilicate [11–20], aluminoborate and sodium aluminoborate glasses [13,14]. Two ways are generally applied in the literature in order to produce the Sm²⁺ charge state in amorphous materials, namely heating in the presence of reducing gases [15,16] or different irradiations like X-ray [17] γ- [14,18] and laser pulses [11,13]. In the glass heated in reducing atmosphere H₂, molecules deplete the oxygen ions surrounding Sm³⁺, resulting in the formation of Sm²⁺ ions:

2Sm³⁺ + O²⁻ + H₂ = 2Sm²⁺ + H₂O [10].

Following the irradiation by focused femtosecond laser (fs-laser pulses) [13] or X- and γ-ray irradiation [14,17], free electrons and holes are created in the glass. Some electrons can be trapped by the Sm³⁺ ions, leading to the formation
of Sm\(^{2+}\) while holes are mainly trapped by oxygen ions bounding with Al ions in case of aluminosilicate glasses [20] or by nonbridging oxygen ions as well as by tetrahedral coordinated boron atoms in case of sodium aluminoborate glasses [13,14].

Recently we studied optical properties and the reduction processes of Sm\(^{3+}\) ions into Sm\(^{2+}\) by \(\gamma\)-irradiation in aluminoborosilicate glasses [18]. We found also that reversible conversion of Sm charge state takes place under \(\beta\)-irradiation [21]. From our experimental data we supposed that the conversion can result in modifications of Sm local environment.

In continuation of our recent investigations the paper presents the data on spectroscopic studies in pristine and \(\beta\)-irradiated Sm-doped aluminoborosilicate glasses in dependence on samarium oxide concentration and irradiation doses. The goal of this work is to analyze the process of Sm\(^{3+}\) reduction in the high dose regions (>10\(^8\) Gy) for different Sm content and in particular to understand the effect of the reduction process on both defect creation processes and structural changes under irradiation. For that purpose, we carried out the combined study of changes in the environment around Sm ions, monitored with luminescence spectra. At the same time glass structural peculiarities under \(\beta\)-irradiation have been studied using Raman and electron paramagnetic resonance (EPR) spectroscopies.

2. Experimental

For the glass synthesis we used the same protocol as in [18,21]. The nominal compositions of the glasses are given in Table 1. Precision of the mass measuring process was determined by the weighting machine uncertainty. Magnitude of the systematic error does not exceed 10 mg that was less than 0.05% of each component used for glass preparation. The mixture was crushed to a fine powder and homogeneous mixing was ensured. The homogeneous powder was put in a Pt crucible and was gradually heated to 1500°C in an electric furnace during 14 h at ambient atmosphere. The melting was then poured on a copper plate. In order to favour homogenous distribution of Sm into the glasses, another 2 hours melting at 1500°C was effected and the samples were then grinded and mixed again into a homogeneous state. After quenching, glass samples were annealed at 500°C in order to decrease strain. Samples of 0.5 mm thickness were irradiated using 2.5 MeV electrons 

Table 1

<table>
<thead>
<tr>
<th>Sm(_2)O(_3) (wt%)</th>
<th>Base 5 oxide borosilicate glass composition (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Si(_2)O(_3)</td>
</tr>
<tr>
<td>0.92</td>
<td>54.47</td>
</tr>
<tr>
<td>1.83</td>
<td>53.97</td>
</tr>
<tr>
<td>2.71</td>
<td>53.48</td>
</tr>
<tr>
<td>4.44</td>
<td>52.53</td>
</tr>
</tbody>
</table>

... during irradiation was maintained around 50 °C by water cooling of the sample holder and all samples were exposed to different irradiation doses between 8 \(\times\) 10\(^5\) and 4 \(\times\) 10\(^6\) Gy. Luminescence and Raman spectra were collected after irradiation on a Labram HR micro-spectrometer using the 514.5 nm line of an Ar\(^+\) laser. Experiments were carried out through \(\times\)100 Olympus objective and a laser power of 80 mW on the sample was used to avoid significant heating of the samples. All Raman spectra of pristine and \(\beta\)-irradiated silica glass samples have been normalized to the intensity of the band near 460 cm\(^{-1}\).

EPR spectra were obtained using a X band \((v \approx 9.420 \text{ GHz})\) EMX Bruker spectrometer with a 100 kHz field modulation, 1 G amplitude modulation and 1 mW microwave power. All EPR spectra have been normalized to the samples mass. Error estimation has been done for all data obtained taking into account contribution of the random and systematic errors. Systematic error included uncertainty in mass measuring. Mass measurement uncertainty was of 0.1 mg. In order to minimize the random error measurements of the spectra were repeated 10 times. All uncertainties have been considered and displayed in the table and on the data in the figures. The microwave frequency has been determined using a Hewlett Packard 5352B frequency counter.

3. Results

Fig. 1 shows luminescence spectra of 3 wt% Sm\(_2\)O\(_3\) doped aluminoborosilicate glass before and after \(\beta\)-irradiation with different doses from 10\(^5\) to 4 \(\times\) 10\(^6\) Gy. Before irradiation the glass exhibits sharp luminescence bands at 563, 600, 646 and 710 nm, which are assigned to the \(^{4}\text{G}_{5/2}–^{6}\text{H}_7/2\) transitions of Sm\(^{3+}\) (with \(J = 5/2, 7/2, 9/2, 11/2\), respectively [22], while in glasses exposed to \(\beta\)-irradiation new luminescence lines appeared for long wavelengths at 680, 710 and 727 nm are assigned to the \(^{4}\text{D}_0–^{6}\text{F}_2\) transitions of Sm\(^{2+}\) ions (with \(J = 0,1,2\), respectively [23]). Thus, it is clear that Sm\(^{3+}\) ions are reduced during \(\beta\)-irradiation. Fig. 2 depicts the Sm\(^{2+}\) fraction, \(\eta_{\text{Sm}^{2+}} = (I_{\text{Sm}^{2+}}/(I_{\text{Sm}^{2+}} + I_{\text{Sm}^{3+}}))\), estimated from the measured luminescence spectra as a function of irradiation dose. The luminescence intensities of Sm\(^{2+}\) and Sm\(^{3+}\), denoted as \(I_{\text{Sm}^{2+}}\) and \(I_{\text{Sm}^{3+}}\), respectively, are determined as the area of the \(^{4}\text{D}_0–^{6}\text{F}_{0,1,2} (\text{Sm}^{2+})\) and \(^{4}\text{G}_{5/2}–^{6}\text{H}_{7/2,9/2} (\text{Sm}^{3+})\) transitions. It is apparent from this figure that reduction of Sm\(^{3+}\) ions is increased with the increase of the dose and this reduction processes
seem to be linear as a function of log(dose) for all Sm$_2$O$_3$ doping considered. Moreover, we observed an almost complete disappearance of the Sm$^{3+}$ luminescence lines for doses as high as $10^9$ Gy (see Fig. 1). This result could therefore be correlated to a complete conversion of Sm$^{3+}$ into Sm$^{2+}$ ions after irradiation. Fig. 3 displays luminescence spectra for Sm-doped aluminoborosilicate glasses irradiated with the highest dose in dependence on Sm$_2$O$_3$ content. The evolution of $\eta_{\text{Sm}^{2+}}$ is plotted as a function of samarium concentration in Fig. 4. From these figures, it can be observed that the efficiency of the reduction processes occurring during irradiation depends also on the Sm$_2$O$_3$ content, although the dependence is not clear yet. For example, at the highest irradiation dose ($4 \times 10^9$ Gy) the intensity of Sm$^{3+}$ luminescence lines shows a trend to increase until 3 wt% of Sm$_2$O$_3$. But this behaviour is not analysed for all doses studied.

The X band-EPR spectra for $\beta$-irradiated aluminoborosilicate glass doped with different Sm concentrations are illustrated in Fig. 5. We found that intensity of the EPR signal attributed to defects is decreased by the addition of Sm$_2$O$_3$ at all doses we have used (insertion in Fig. 5). This behavior has also been observed previously for other rare-earth dopant in glass like gadolinium (after
β-irradiation) [24] and samarium (after γ-irradiation) [18]. We have only considered EPR defect lines in this work because the $g$ values of Sm$^{3+}$ ions ($g_{||} \sim 0.11$, $g_{\perp} \sim 0.714$) [25] is out of the magnetic field range of our spectrometer. Raman spectra of β-irradiated glasses in comparison with pristine samples are presented in Fig. 6. A shift ($\approx 20 \text{ cm}^{-1}$) of the Si–O–Si bending vibration modes (~460 cm$^{-1}$) showing a decrease of the average Si–O–Si angle is observed in all Sm-doped β-irradiated glasses. Moreover, a band at 600 cm$^{-1}$, corresponding to the breathing mode of three membered SiO$_4$ rings appears under irradiation. As it can be seen, irradiation results in a decrease of the $Q_2$ at 980 cm$^{-1}$ species relative to $Q_1$ at 1100 cm$^{-1}$ species (where $Q_n$ species correspond to SiO$_4$ tetrahedra with $n$ bridging oxygens) showing an increase of the glass polymerisation, but it is difficult to quantify this result because of significant overlap of the Raman spectrum and the tail of the first luminescence band of Sm$^{3+}$ ions. The structural changes under irradiation are similar to those previously observed in borosilicate glass without rare-earth doping [26], though with Sm adding (Sm$_2$O$_3$ doping) the modifications in glass structure are not so noticeable and become weaker (have tendency to the blockage). For example the Si–O–Si bending vibration modes shift decreases with the increase of the Sm content as it is shown in insertion in Fig. 6 leading to the Si–O–Si average angle increase and densification diminution.

4. Discussion

As it is mentioned above the Sm$^{3+}$ ion reduction can be obtained by using different types of ionizing radiation (X-ray, γ- or fs-laser) [13,14,19]. To the best of our knowledge, no effect of this process on the structural changes in glass host matrix has been discussed. Our recent investigations showed that the reduction is not always accompanied by the modifications in glass structure [27]. Thus, a question of great importance is: is there some general law for the interplay of RE reduction with structural changes in glass under irradiation?

The reduction of Sm$^{3+}$ into Sm$^{2+}$ can be observed from measurements of the luminescence spectra of glasses studied before and after β-irradiation (Fig. 1). Thus, it is concluded that β-irradiation is effectively being used to reduce Sm$^{3+}$ ions into Sm$^{2+}$ ions in the glass matrix. Moreover, the increasing of the irradiation dose results in an almost complete transformation of Sm$^{3+}$ into Sm$^{2+}$ ions as it is shown in Figs. 1 and 3 for 3 wt% Sm$_2$O$_3$ content. In fact, in case of the fs-laser pulses with a high intensity, or X- or γ-irradiations, only the partial reduction of the Sm$^{3+}$ ions was observed [13,14,19]. Nonequivalence in the dose in case of γ- and β-irradiation (~10$^5$ and ~10$^9$ Gy, respectively) seems to be a reason for such difference in the reduction efficiency. We investigated the evolution of the reduction process with samarium concentration for all irradiation doses (Fig. 4). It is well-known that RE ions luminescence intensity is often concentration dependent. In the previous paper we discussed the effect of Sm$_2$O$_3$ content on Sm$^{3+}$ ions luminescence intensity in aluminoborosilicate glasses [18]. At concentration of Sm$_2$O$_3$ higher than 0.5 wt% the nonradiative energy transfer between Sm$^{3+}$ ions arising from dipole–dipole interaction was found to be responsible for the luminescence quenching. On the other hand, no detectable effect of samarium...
oxide content on Sm$^{2+}$-luminescence intensity was observed (Fig. 3). Therefore the relative ratio of Sm$^{2+}$ ions formed during irradiation ($\eta_{Sm^{2+}}$) revealed non-clear dependence on samarium concentration presented in Fig. 4. This evolution can not be explained by the influence of host glass like it was found in [19] where the relative ratio ($\eta_{Sm^{2+}}$) in aluminosilicate glasses is increased by the addition of Al$^{3+}$ ions, because in our case the base glass matrix composition was the same for all samples. The presented data have no correlation with dependence of Sm$^{2+}$ relative ratio on Sm$_2$O$_3$ content in $\gamma$-irradiated aluminoborosilicate glasses where the reduction of Sm$^{3+}$ ions is decreased by the increase of Sm-doping level for the irradiation doses up to the 1000 kGy [18]. Sm$^{3+}$ reduction process (electron trapping) under ionizing radiation is usually associated with processes of defects creation acting as hole trap [13,14,19]. Therefore, it is necessary to take into consideration the behaviour of the defect centers in addition to the rare-earth ions.

The observed EPR signal for irradiated samples presented in Fig. 5 shows well-known lines for the hole centers trapped in oxygen ions bonding with B ions (so-called BOHC) typical for this glass [28]. In contrast with non-clear dependence the $\eta_{Sm^{2+}}$ on level of Sm-doping, the amount of hole defects decreases when dopant’s concentration increases (inset of Fig. 5). The decrease of paramagnetic defects concentration can be due to the fact that excitons produced during ionizing radiation can support dynamical balance between the two charge states of Sm ions (Sm$^{3+}$ + (h$^0$/e$^-$) => Sm$^{2+}$ + h$^0$ => Sm$^{3+}$ or Sm$^{2+}$ + (h$^0$/e$^-$) => Sm$^{3+}$ + e$^-$ => Sm$^{2+}$). The same results have also been observed in $\gamma$-irradiated Sm$^{3+}$-doped alumino-borosilicate glasses [18].

But in case of $\beta$-irradiation, defect concentration analyzed by EPR doesn’t seem to be in accordance with the quantity of Sm$^{2+}$ produced during irradiation at higher doses. Indeed the amount of the trapped electrons (Sm$^{2+}$) observed by luminescence experiments is a few order of magnitude larger than the amount of the holes trapped by nonbridging oxygens detected by EPR ($10^{16} - 10^{17}$ spin/cm$^3$). Even if holes can be trapped in diamagnetic defects observed by absorption measurements, the reduction processes at higher doses cannot be only correlated with the production of holes defects as it is commonly explained in literature. A possible explanation of the disbalance between electron and hole traps could be gas production during irradiation (O$_2$, CO, CO$_2$) corresponding to an oxidation of structural oxygen and impurities like residual carbonates counterbalancing the reduction of Sm$^{3+}$ during irradiation. $\beta$-irradiation experiments in H$_2$ sealed tube [29] are planned in order to verify this assumption by measuring as a function of Sm$_2$O$_3$ content and the integrated dose the nature and the quantity of gas.

Effect of Sm$_3$O$_3$ content on structural modifications in aluminoborosilicate glass which take place only under $\beta$-irradiation is not so easy to quantify. Indeed, the anomalies in Raman spectra (Fig. 6) are due to the overlap with the tail of the first luminescence band of the Sm$^{3+}$ ions. This implies that we are not able to determine precisely the changes of the position of the bands at value for Raman shift higher than 1000 cm$^{-1}$ corresponding mainly to $Q_n$ species (1000–1200 cm$^{-1}$), stretching vibration modes of B-O bonds (1350–1450 cm$^{-1}$) and molecular oxygen stretching vibration modes (1550 cm$^{-1}$). It is possible however to measure the evolution for the band attributed to Si–O–Si bending vibration modes (at 460 cm$^{-1}$). With increasing of the dopant levels, the shift between irradiated and pristine (inset of Fig. 6) tends to diminish which results in an increase of the average Si–O–Si angle in irradiated Sm-doped glasses. Changing of the average Si–O–Si angle can be correlated with changes in glass densification under $\beta$-irradiation. This decrease of structural changes under irradiation with the Sm$_2$O$_3$ content is similar to the influence of Fe$^{3+}$ doping in soda lime glass composition [27]. For both glass compositions, addition of Fe$^{3+}$ or Sm leads to the reduction of the dopant ion, a strong decrease of defect production and other structural changes under irradiation. On the contrary, when ion reduction process under irradiation is small like in Gd-doped glasses [24], the influence of doping on the defect content and structural changes is also negligible. Taking into account all mentioned above facts it is apparent that Sm ions play a complex role in the structure of $\beta$-irradiated alumino-borosilicate glass and the reduction mechanism strongly affects the structural modifications following by irradiation. It is known for example that Sm$^{3+}$ ion can be considered as an electron acceptor [19]. The authors [19] suggest also that Sm$^{2+}$ ions are supposed to have the similar effect on the glass structure as Eu$^{3+}$ ions and act as network modifier ions in the aluminosilicate glasses. Moreover, according to their fluorescence line narrowing (FLN) spectroscopy data, the Sm$^{3+}$ ions can be located in two different sites which are not similarly reduced to Sm$^{2+}$. The effect of reduction on Sm average coordination number and the Sm ion local structure investigated by using $^{27}$Al MAS NMR spectroscopy and X-ray radial distribution function (RDF) analysis are discussed in [30]. The authors found that the average coordination number Sm ion in aluminosilicate glass slightly increase from 7.1 (for Sm$^{3+}$ ion) to 8.5 (for Sm$^{2+}$ ion) after heat-treatment in reducing atmosphere. Therefore, the question of coordination changes around Sm during ionizing radiation in the aluminoborosilicate glasses remains unknown and FLN and XAFS experiments should be planned in order to go further in this study.

5. Conclusion

The optical properties of $\beta$-irradiated Sm-doped aluminoborosilicate glasses were investigated by luminescence, EPR and Raman spectroscopies. We found that Sm$^{3+}$ ions can be completely reduced into Sm$^{2+}$ by $\beta$-irradiation with doses higher than $10^3$ Gy. The EPR measurements have shown that the hole defect production strongly depends on the dopant amount and has tendency to diminish with
the increase of Sm content. With the addition of Sm$_2$O$_3$, a decrease of the structural changes under irradiation (decrease of average Si–O–Si angle, increase of glass polymerisation) has been observed by Raman spectroscopy. Absence of correlation between the quantity of trapped electrons and holes produced during irradiation let us suggest that hole defects are not the counterpart of Sm$^{3+}$ ions reduction processes and another mechanism, like gas production, must be taken into account in order to explain the results obtained by luminescence.

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