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# Reduction of $\text{Eu}^{3+}$ to $\text{Eu}^{2+}$ in aluminoborosilicate glasses under ionizing radiation

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## Abstract

$\text{Eu}_2\text{O}_3$ -doped aluminoborosilicate glasses were prepared by melting in air at high temperature ( $\sim 1500^\circ\text{C}$ ). It was shown by luminescence and Electron Paramagnetic Resonance measurements that both  $\text{Eu}^{3+}$  and  $\text{Eu}^{2+}$  ions can exist simultaneously in the glass matrix studied after glass synthesis as well as after exposure to ionizing radiation. Increase of total  $\text{Eu}_2\text{O}_3$  concentration leads to the increase of  $\text{Eu}^{3+}$  luminescence intensity while the luminescence intensity of  $\text{Eu}^{2+}$  ions tends to reduce. Although as it is seen by Electron Paramagnetic Resonance spectroscopy amount of  $\text{Eu}^{2+}$  ions inside the glass is raised with total  $\text{Eu}_2\text{O}_3$  concentration. The difference in the results of both spectroscopies is explained in terms of energy transfer from  $\text{Eu}^{2+}$  to  $\text{Eu}^{3+}$  leading to an  $\text{Eu}^{2+}$  luminescence quenching. Irradiation results in the increase of reduced  $\text{Eu}^{2+}$  quantity detected by Electron Paramagnetic Resonance measurements. It was shown that  $\text{Eu}^{2+}$  ions are located in both high ( $g \sim 4.6$ ) and low symmetry ('U' spectrum) sites in the structure of aluminoborosilicate glasses glass. The content of  $\text{Eu}^{2+}$  ions occupied these sites increases by the irradiation dose increase manifesting the presence of strong reduction process  $\text{Eu}^{3+} \rightarrow \text{Eu}^{2+}$ .

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keywords : borosilicate glasses, rare-earth reduction, irradiation, luminescence, EPR

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## 1. Introduction

It is known that rare-earth (**RE**) elements can be embedded as fission products in the glasses used for the immobilization of high-level nuclear wastes (HLW) [1]. At the same time, some RE ions can be considered as chemical surrogates of minor actinides and therefore could modeled the actinide environment for the simulation of the behavior of real vitrified radioactive actinides [2,3]. For that purpose simplified oxide nuclear glasses, doped with different RE elements, were exposed to  $\beta$ -irradiation in order to simulate the consequences of  $\beta$ -decay and predict influence RE ions on structure of host matrices [4-6]. Europium is representative of actinides as the chemical properties of  $\text{Eu}^{3+}$  are very similar to those of trivalent actinides and in particular to  $\text{Am}^{3+}$ . Furthermore,  $\text{Eu}^{3+}$  can be used as a local structural probe with different spectroscopic methods [7,8].

The coexistence of both  $\text{Eu}^{3+}$  and  $\text{Eu}^{2+}$  ions has been found in some phosphors glasses or films during melting or prepared under reduction atmosphere [9-14]. The reducing atmosphere, such as  $\text{H}_2$  or  $\text{CO}$ , is generally needed to reduce  $\text{Eu}^{3+}$  to  $\text{Eu}^{2+}$  during the synthesis of  $\text{Eu}^{2+}$  doped luminescent materials. However, the preparation of  $\text{Eu}^{2+}$  doped materials in air is more convenient than in reducing atmosphere. Some research works on reduction of  $\text{Eu}^{3+}$  into  $\text{Eu}^{2+}$  in air has been reported in Eu doped  $\text{Al}_2\text{O}_3\text{-SiO}_2$  glasses [15],  $\text{MO-B}_2\text{O}_3$  glasses ( $\text{M} = \text{Ba}, \text{Sr}, \text{and Ca}$ ) [16] and aluminoborosilicate (**ABS**) glasses [17].

Taking into account, that  $\text{Eu}^{3+}$  ion is an active electron trap [18], it is apparent to consider that ionizing radiation such as  $\gamma$ -rays [18-21] or irradiation with femtosecond laser

pulses [22,23] results in the formation of  $\text{Eu}^{2+}$  ions after  $\text{Eu}^{3+}$  reduction. Besides, our recent investigations on irradiated Sm-doped ABS glasses have confirmed the presence of almost complete  $\text{Sm}^{3+}$  reduction by luminescence measurements in  $\beta$ -irradiated ABS glasses at the highest irradiation doses ( $10^9$  Gy) [5].

In continuation of our recent studies, we investigated  $\text{Eu}^{3+}$  reduction process in pristine and exposed to  $\beta$ -irradiation ABS glasses doped with  $\text{Eu}_2\text{O}_3$ . The influence of europium concentration as well as irradiation integrated dose on both optical and structural properties of Eu-doped ABS glasses are considered in the present paper.

## 2. Experimental methods

The nominal general composition of the ABS glass was (in mol%): 59.77 %  $\text{SiO}_2$ , 4.00 %  $\text{Al}_2\text{O}_3$ , 22.41 %  $\text{B}_2\text{O}_3$ , 12.12 %  $\text{Na}_2\text{O}$ , 1.70 %  $\text{ZrO}_2$ . Eu-doped ABS glasses were prepared by adding to the base glass different amounts of **europium oxide  $\text{Eu}_2\text{O}_3$**  (from 0.1 to 1 mol%). The dried mixed powders were first heated at  $750^\circ\text{C}$  in a Pt crucible during 10 hours for removing carbonate from the reagents. Then, it was melted at  $1500^\circ\text{C}$  for one hour and quenched in air. The different glasses were annealed at  $500^\circ\text{C}$  during few hours to release strains. Each glass was analyzed by X-Ray diffraction, which confirms the amorphous character of glass.

All glasses were  $\beta$ -irradiated with 2.5 MeV electrons ( $10 \mu\text{A}$ ) provided by a Van de Graaff accelerator (LSI, Palaiseau, France) at different integrated doses from  $10^6$  to  $2 \cdot 10^9$  Gy. **Electron Paramagnetic Resonance (EPR)** measurements were conducted at room temperature on a X band ( $\nu = 9.420$  GHz) EMX Brücker EPR spectrometer using a 100 kHz field modulation, 3 gauss of amplitude modulation and an applied microwave power of 1 mW (defect EPR line) and 20 mW for  $\text{Eu}^{2+}$  resonances.. The EPR spectra of all irradiated RE-

doped ABS glasses have been normalized to the same receiver gain and to a 100 mg sample weight. Paramagnetic defects total content has been estimated by the area under the defect absorbance EPR spectrum. A maximum error of 10 % has been considered in this work taking into account uncertainties in the irradiated glass samples weight measurement, the sample positioning inside spectrometer cavity and defect absorbance EPR spectrum area computation or EPR line intensity measurement.

### 3. Results

**Fig.1** shows luminescence spectra of pristine ABS glass doped with 0.2 mol% of  $\text{Eu}_2\text{O}_3$  excited with different wavelength. The emission between 550 and 620 nm can be attributed to well-known transitions from  $^5\text{D}_0$  to  $^7\text{F}_J$  ( $J = 0, 1$  and  $2$ ) levels of  $\text{Eu}^{3+}$  [15,17]. Appearance of the broad band positioned between 350-500 nm can be assigned to the 5d - 4f transition of  $\text{Eu}^{2+}$  ions [15,17]. The observed emission bands under different wavelength of excitation are basically the same but the contribution of both  $\text{Eu}^{3+}$  and  $\text{Eu}^{2+}$  emission intensity is different. It can be seen from **Fig. 1** that excitation in the  $\text{Eu}^{2+}$  band (330 and 350 nm) results in the higher luminescence intensity of  $\text{Eu}^{2+}$  ions while  $\text{Eu}^{3+}$  ions luminescence is negligible. Indeed, 5d band of  $\text{Eu}^{2+}$  is observed in the Eu doped ABS glass excitation spectrum monitored at 420 nm. One can observe in Fig. 2 that  $^8\text{S}_{7/2} \rightarrow 5\text{d}$  band consists of two component  $t_{2g}$  (320 nm) and  $e_g$  (370 nm) splitted by the crystal field around  $\text{Eu}^{2+}$  ions. At the same time a weak band at 320 nm can also be distinguished in the  $\text{Eu}^{3+}$  excitation spectrum, indicating the presence of energy transfer (**ET**) from  $\text{Eu}^{2+}$  ions 5d level to the  $\text{Eu}^{3+}$  ions 4f levels. It is apparent from Fig. 3, that the overlap between broad emission of  $\text{Eu}^{2+}$  and the different excitation bands of  $\text{Eu}^{3+}$  can result in energy transfer from  $\text{Eu}^{2+}$  to  $\text{Eu}^{3+}$  ions increasing the  $\text{Eu}^{3+}$  emission efficiency. Indeed, as it can be seen from **Fig. 4**, the increase of  $\text{Eu}_2\text{O}_3$  content into the ABS glass leads

to the quenching of  $\text{Eu}^{2+}$  luminescence while the intensity of  $\text{Eu}^{3+}$  emission bands is increasing.

Additional evidence of  $\text{Eu}^{2+}$  ions formation during Eu doped ABS glass synthesis is provided by EPR spectra shown in **Fig. 5** for sample doped with 0.6 mol%  $\text{Eu}_2\text{O}_3$  doped ABS glasses. It is known that  $\text{Eu}^{3+}$  ion is not paramagnetic one and therefore does not make contribution in EPR signal. By contrary,  $\text{Eu}^{2+}$  ion has the electronic spin ( $S$ ) and nuclear spin ( $I$ ) are  $7/2$  and  $5/2$ , respectively [24] and can be easily studied by EPR spectroscopy at room temperature. It should be noted that  $\text{Eu}^{2+}$  ion has the same electronic configuration as  $\text{Gd}^{3+}$  ion and, as expected, EPR spectra of  $\text{Eu}^{2+}$ -doped ABS glasses are similar to those of  $\text{Gd}^{3+}$ -doped ABS glasses [4]. Moreover, obtained EPR spectra of Eu doped ABS glasses are in good agreement with those published for Eu doped borophosphate glass and fluorobromozirconate glass ceramics [25,26].

At the same time some specific features can be noticed in the EPR spectra of both pristine and irradiated Eu-doped ABS glass. As in can be seen from **Fig.5** for pristine samples all observed EPR lines of so-called “U” spectrum (at  $g \sim 6.0$  ( $\sim 1154$  G),  $g \sim 2.8$  ( $\sim 2570$  G) and  $2.0$  ( $\sim 3427$  G)) are broadening enough in comparison with those in irradiated glass samples. In addition, the intensity ratio between the  $g \sim 6.0$  and  $2.8$  EPR lines of the U spectrum is observed to be increasing for irradiated  $\text{Eu}^{2+}$  doped glasses comparing to  $\text{Gd}^{3+}$ -doped glass. Besides, the relative proportion between intensities of EPR line at  $g \sim 4.6$  ( $\sim 1628$  G) and of the components of “U” spectrum in irradiated Eu-doped ABS glasses reveals an increase by 3 orders of magnitude in comparison with the same ratio obtained in Gd-doped ABS glass (**Fig.5**). Finally for all irradiated samples, an EPR line at  $g \sim 2.3$  ( $\sim 3060$  G) is found to be correlated to some paramagnetic impurity.

**It should be noted that quantity of reduced  $\text{Eu}^{2+}$  ions is affected by the Eu concentration.** It is apparent, that with the increase of  $\text{Eu}_2\text{O}_3$  content in ABS glasses, the

intensity of EPR lines associated with  $\text{Eu}^{2+}$  ions increases, although relative ratio between two  $\text{Eu}^{2+}$  bands ( $g \sim 4.6$  and  $6.0$ ) reveals negligible dependence with doping ion concentration (**Fig. 6**). The evolution of observed  $\text{Eu}^{2+}$  EPR lines at  $g \sim 4.6$  and  $6.0$  is followed by the same tendency with increasing the integrated dose (**Fig. 7**). The EPR lines observed around  $g \sim 2.0$  ( $\sim 3500$  G) detected only in irradiated ABS glasses are attributed to the defects created by ionizing radiation (Fig. 8) [4-6,27]. Two results can be **deduced from Fig. 8**. First, one can see a strong decrease of the radiation defect content with the  $\text{Eu}_2\text{O}_3$  concentration in the glasses (at one integrated dose). In addition to the total defect amount decrease, a diminution of the relative proportion between Bore Oxygen Hole Centers (BOHC) and electron centers ( $\text{E}'$ -defects: electron trapped by silicon atom) [27] is clearly seen in the EPR spectra attributed to radiation defects (Fig. 8).

#### 4. Discussion

Observed luminescence in as-prepared ABS glasses doped with Eu ions can be attributed both  $\text{Eu}^{3+}$  and  $\text{Eu}^{2+}$  ions indicating therefore that glass synthesis in air at high temperature affected the oxidation states of europium in this ABS glass composition. The broad blue emission with maximum at  $\sim 420\text{-}450$  nm (Fig.1) undoubtedly belongs to the transition  $4f^65d \rightarrow 4f^7$  of  $\text{Eu}^{2+}$  ion. Intensity of  $\text{Eu}^{2+}$  ions is increased while the intensity of  $\text{Eu}^{3+}$  drastically decreases with changing of wavelength of excitation **which is apparently related to the fact that the  $\text{Eu}^{2+}$  excitation band is a broad one while  $\text{Eu}^{3+}$  spectrum is characterized by a variety of discrete excitation lines**. Indeed, in the excitation spectrum for the emission at 580 nm (Fig.2) one can see group of 4f intra-configurational transitions from the  $^7\text{F}_0$  level to upper-lying excited states in the region of 350-500 nm and the charge transfer band at 250 nm attributed to the electron transfer from 2p orbitals of  $\text{O}_2^-$  to 4f levels

of  $\text{Eu}^{3+}$  [28]. Nevertheless, under monitoring in 420 nm in the excitation spectrum broad band in the region 250-400 nm corresponding to  $4f^65d \rightarrow 4f^7$  transition in  $\text{Eu}^{2+}$  ion is observed as it is shown in Fig.2. The 4f – 5d excitation band of  $\text{Eu}^{2+}$  ions consists of two components attributed to a splitting of 5d orbitals into  $e_g$  and  $t_{2g}$  components [29]. This separation is in agreement with examination of  $\text{Eu}^{2+}$  absorption spectra in aluminosilicate glasses, where sites of cubic symmetry with 8- and 12-fold coordination are considered resulting in a splitting to  $e_g$  component at lower energy and  $t_{2g}$  component at higher energy [30,31]. Thus, in this ABS glass investigated, the  $e_g$  band being the lowest in energy ( $\sim 370$  nm) indicates that the  $\text{Eu}^{2+}$  ions possess cubic sites with higher symmetry. It is interesting to notice that the appearance of weak band at 320 nm in the excitation spectrum of  $\text{Eu}^{3+}$  can be ascribed to 4f-5d transition of  $\text{Eu}^{2+}$ . Moreover strong overlap between broad blue emission of  $\text{Eu}^{2+}$  and excitation bands of  $\text{Eu}^{3+}$  in the region 350-500 nm is observed as it is seen from Fig.3. Based on these experimental results and taking into account the energy level diagram of the  $\text{Eu}^{2+}$  and  $\text{Eu}^{3+}$  ions [31] it is possible to suppose that energy transfer from  $\text{Eu}^{2+}$  to  $\text{Eu}^{3+}$  can take place. The mechanism of energy transfer is similar to that described in [31, 32]. **The excited in  $4f^65d(e_g)$  state the ion  $\text{Eu}^{2+}$  transfers the energy by means of non-radiative transition  $4f^65d(e_g) \rightarrow {}^8S_{7/2}$  to the ground state resulting in the excitation of  ${}^5D_0$  level of  $\text{Eu}^{3+}$  ion.** We also observed another evidence of energy transfer from  $\text{Eu}^{2+}$  ions to  $\text{Eu}^{3+}$  by measuring the relative ratio between emission intensities for both ions (Fig.4). Indeed, diminution of  $\text{Eu}^{2+}$  emission intensity with simultaneous enhancement of  $\text{Eu}^{3+}$  luminescence as a function of  $\text{Eu}_2\text{O}_3$  concentration is caused by non-radiative relaxation of  $\text{Eu}^{2+}$  ion to the ground state ( ${}^8S_{7/2}$ ) providing energy transfer (resonant or through re-absorption [33]) to  $\text{Eu}^{3+}$  ions.

The occurrence of well known “U” EPR spectrum described for  $\text{Gd}^{3+}$  doped glasses [34-43] in both as-prepared and irradiated Eu-doped ABS glass clearly shows the presence of  $\text{Eu}^{2+}$  ions with the same electronic configuration like  $\text{Gd}^{3+}$  ions (Fig.5). Although, a specific



broadening of the  $\text{Eu}^{2+}$  EPR lines width at  $g \sim 2.8$  and  $2$  for pristine as-prepared ABS glasses as well as different ratio between the intensities of the components of “U”-spectrum and EPR line at  $g \sim 4.6$  for irradiated ABS glasses comparing to those of  $\text{Gd}^{3+}$  EPR lines can be noticed (Fig.5). We assume that these differences in could be due to a different local environment in terms of disorder around an average site of  $\text{Eu}^{2+}$  ions.

Since  $\text{Eu}^{2+}$  ion is equivalent for EPR to  $\text{Gd}^{3+}$  ion, it is expected to observe similar EPR spectra for both doping ions. Indeed, comparing the EPR data for both Gd- [4] and Eu-doped ABS glass we can notice similarities. First the appearance of “U” spectrum ( $g \sim 2.0, 4.6$  and  $6.0$ ) as well is less ordinary observed EPR band at  $g \sim 4.6$ . The origin of this spectrum for  $\text{Gd}^{3+}$  doped glasses has been discussed by several authors [34-40]. The more complete and thorough treatment have been effected by Brodbeck and Iton [40, 41]. They pointed out that the EPR features at  $g \sim 2.8$  and  $g \sim 6.0$  are always occurred together with similar relative intensity and that all bands of “U” spectrum ( $g \sim 2.0, g \sim 2.8$  and  $g \sim 6.0$ ) are assigned to transitions of  $\text{Gd}^{3+}$  ions in one site. On the contrary, EPR signal at  $g \sim 4.8$  is corresponding to a  $\text{Gd}^{3+}$  site different from the one observed in the “U”-spectrum [36,42,43]. Indeed, our recent study of irradiated  $\text{Gd}^{3+}$ -doped ABS glass clearly showed that the observed changes in the EPR spectra in dependence on the integrated dose can only be interpreted with two  $\text{Gd}^{3+}$  environments in the glass investigated [4].

However, it was underlined in [29] that  $\text{Eu}^{2+}$  and  $\text{Gd}^{3+}$  ions do not occupy similar sites. It is marked that the ligand field splitting of the  $4f^{n-1}5d$  excited configurations is different for trivalent and divalent ions. Thus, Ebendorff-Heidepriem et al. pointed out that in the case of  $\text{Eu}^{2+}$  ions, the splitting of the  $5d$  orbitals into  $e_g$  and  $t_{2g}$  orbitals suggests cubic RE sites of higher symmetry while Azzoni et al. [44] inferred the presence of at least one site for  $\text{Gd}^{3+}$  ion with symmetry lower than cubic and coordination number higher than  $6$  [34-40]. At the same time, Furnis et al. affirm that the higher  $\text{Eu}^{2+}$  crystal-field terms reflect greater departures

from spherical symmetry than it is occurred for the  $Gd^{3+}$  ions [45]. Coey et al. concluded that divalent europium in different fluorozirconate glass is occupied not good defined sites with a range of coordination numbers from 8 to 12 as it was confirmed by optical investigations [30,31], whereas the sites occupied by a trivalent rare-earth ion are more uniform [46].

Nevertheless, based on our EPR experimental results on  $Eu^{2+}$  ions and previous EPR analysis of  $Gd^{3+}$  ions behavior in ABS glass we can conclude that these RE ions occupy equivalent positions (in terms of the environment symmetry) in the glass investigated. Indeed, the presence of two  $Gd^{3+}$  sites different in symmetry and local environment is apparent: exposure to irradiation reveals not the same evolution of the sites with irradiation dose increase [4]. Moreover relative proportion between sites attributed to  $Gd^{3+}$  ions in position of network former ( $g \sim 4.8$ ) and network modifier ( $g \sim 6.0$ ) is decreased by the increase of  $Gd_2O_3$  concentration [47]. For Eu doped glasses, **the ratio between  $Eu^{2+}$  EPR lines intensities at  $g \sim 6.0$  and  $g \sim 4.6$  ( $I_{g-6.0}/I_{g-4.6}$ ) showed not significant dependence on  $Eu_2O_3$  content (Fig.6) but at the same time **the evolution of these lines as a function of integrated dose reveals the similar tendency** (Fig.7). It is well established in literature that  $Eu^{3+}$  ions are located in two environments in oxide glasses like silicate, borate, borosilicate and aluminoborate [48]. Thus it is logical to suppose that reduction processes of the  $Eu^{3+}$  ions in ABS glasses can produce different  $Eu^{2+}$  sites with different coordination numbers, crystal field strength and covalency between the ligands and  $Eu^{2+}$  ions. Present EPR study revealed the presence of two  $Eu^{2+}$  sites – a high symmetry site corresponding to the line at  $g \sim 4.6$  and a low symmetry site characterized by the  $Eu^{2+}$  “U” EPR spectrum. However equivalent ratio between these sites as a function of doping ion content and their similar behaviour with integrated dose are not clearly understood and can not be explained at the moment requiring further studies. In the case of fluorozirconated glasses doped with Eu, Coey et al. determined by Mossbauer spectroscopy an  $Eu^{2+}$  environment and interpreted  $Eu^{2+}$  site in these glasses as**

a network modifier one [46]. Taking into account this consideration and based on our result presented we assume that the “U” spectrum for  $\text{Eu}^{2+}$  is attributed to a network modifiers location for the  $\text{Eu}^{2+}$  ion.

Amount of defects created under irradiation is decreased by the increase of  $\text{Eu}_2\text{O}_3$  doping level as it was found early for all RE embedded in ABS glass [4-6] and could due. to the fact that electron-hole pairs produced during ionizing radiation support dynamical balance between the two charge states of Eu ions ( $\text{Eu}^{3+} + (\text{h}^0/\text{e}^-) \Rightarrow \text{Eu}^{2+} + \text{h}^0 \Rightarrow \text{Eu}^{3+}$  or  $\text{Eu}^{2+} + (\text{h}^0/\text{e}^-) \Rightarrow \text{Eu}^{3+} + \text{e}^- \Rightarrow \text{Eu}^{2+}$ ) rather than participate in the rupture of the bonds between the atoms forming glass network. The same results have also been observed in  $\beta$ -irradiated aluminoborosilicate glasses doped with  $\text{Sm}^{3+}$  or  $\text{Ce}^{4+}$  ions [5,6]. It is interesting to notice also the well-resolved structure of the EPR line attributed to the Boron Oxygen Hole Center (BOHC) defects (Fig.8), while the radiation defect ERP signal in aluminoborosilicate glasses doped with  $\text{Gd}^{3+}$  ions considered as an analogue to  $\text{Eu}^{2+}$  ion reveals no any structure due to preferentially distribution in the borate environment [4]. On the contrary from the results of Fig.8 we can conclude that that  $\text{Eu}^{2+}$  ions produced during irradiation are distributed more homogeneously in the glass studied and located not in the vicinity of BOHC centers. Except total radiation defect diminution with increase of  $\text{Eu}_2\text{O}_3$  concentration one can see the decrease of relative proportion between hole (BOHC) and electron (E') defects in dependence on  $\text{Eu}_2\text{O}_3$  concentration. It is well-known that  $\text{Eu}^{3+}$  ion is a good electron trap, therefore this ion can competes with intrinsic electron traps for the defects production and reduces significantly the number of electron defects. As a matter of fact, this result is reflected in Fig. 8 where the intensity of the EPR line belonging to E' defect decreases as a function of  $\text{Eu}_2\text{O}_3$  doping content and becomes negligible for ABS glasses doped with 0.4 mol% europium oxide and higher.

## 5. Conclusion

The effect of europium concentration and irradiation dose on the  $\text{Eu}^{3+} \rightarrow \text{Eu}^{2+}$  reduction in aluminoborosilicate glasses has been studied. It is shown that both  $\text{Eu}^{3+}$  and  $\text{Eu}^{2+}$  ions can coexist simultaneously in the as-prepared glass. Luminescence properties of  $\text{Eu}^{2+}$  ions are found to be concentration-dependent. Energy transfer between  $\text{Eu}^{2+}$  and  $\text{Eu}^{3+}$  ions is assumed to be responsible for the  $\text{Eu}^{2+}$  emission quenching and enhancement of  $\text{Eu}^{3+}$  luminescence efficiency. At the same time Electron Paramagnetic Resonance measurements confirm the strong increase of the  $\text{Eu}^{2+}$  ions quantity in aluminoborosilicate glasses with increase of  $\text{Eu}_2\text{O}_3$  concentration as well as with irradiation dose. Moreover, observed Electron Paramagnetic Resonances let us suppose that the position of  $\text{Eu}^{2+}$  ions in aluminoborosilicate glass could be associated with both network modifier (low symmetry) and network former (high symmetry) sites. Finally, it is postulated that the radiation effects on the structure of aluminoborosilicate glass in particular creation of radiation defects can be essentially minimized by the europium doping.

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## Figure Captions

Figure 1: Luminescence spectra of pristine as-prepared Eu-doped ABS glass (0.2 mol% of  $\text{Eu}_2\text{O}_3$ ) in dependence on excitation wavelength (Xe lamp)

Figure 2: Excitation spectra for  $\text{Eu}^{2+}$  and  $\text{Eu}^{3+}$  ions monitored at 420 and 580 nm, respectively, measured for pristine as-prepared Eu-doped ABS glass (0.2 mol% of  $\text{Eu}_2\text{O}_3$ )

Figure 3: Overlap of  $\text{Eu}^{2+}$  luminescence spectrum (**350 nm**) with  $\text{Eu}^{3+}$  excitation spectrum of pristine as-prepared Eu-doped ABS glass (**580 nm**) (0.2 mol% of  $\text{Eu}_2\text{O}_3$ )

Figure 4: **Evolution of the luminescence spectra ( $\lambda_{\text{ex}} = 266\text{nm}$ , Xe lamp) of pristine as-prepared Eu-doped ABS glass on  $\text{Eu}_2\text{O}_3$  concentration; in inset – the intensity ratio  $\text{Eu}^{2+}/\text{Eu}^{3+}$  as a function of  $\text{Eu}_2\text{O}_3$  content**

Figure 5: EPR spectra of pristine and irradiated Eu- and Gd-doped ABS glass (0.6 and 0.57 mol% of  $\text{Eu}_2\text{O}_3$  and  $\text{Gd}_2\text{O}_3$ , respectively)

Figure 6: **Ratio between EPR line intensities** at  $g \sim 4.6$  and  $g \sim 6.0$  as a function of  $\text{Eu}_2\text{O}_3$  concentration

Figure 7: Dependence of EPR band intensity of Eu-doped ABS glass at  $g \sim 4.6 - a$  and  $g \sim 6.0 - b$  on irradiation dose



Figure 8. Evolution of EPR defects concentration on  $\text{Eu}_2\text{O}_3$  concentration in  $\beta$ -irradiated glasses ( $5.3 \cdot 10^8$  Gy); **in inset – radiation defect content as a function of  $\text{Eu}_2\text{O}_3$  concentration**

Figure 1

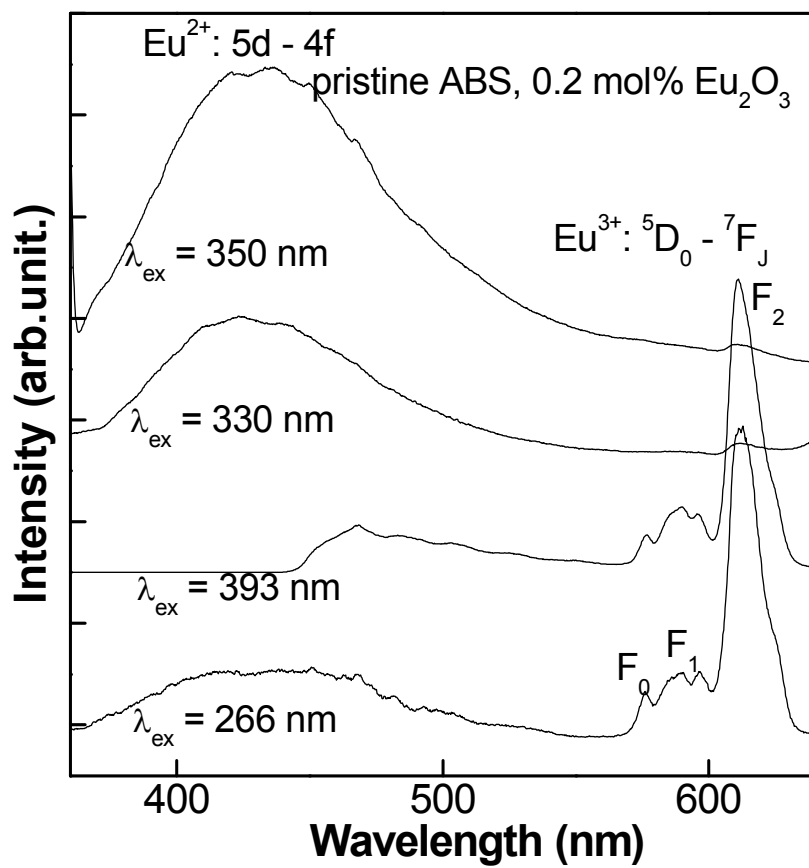


Figure 2.

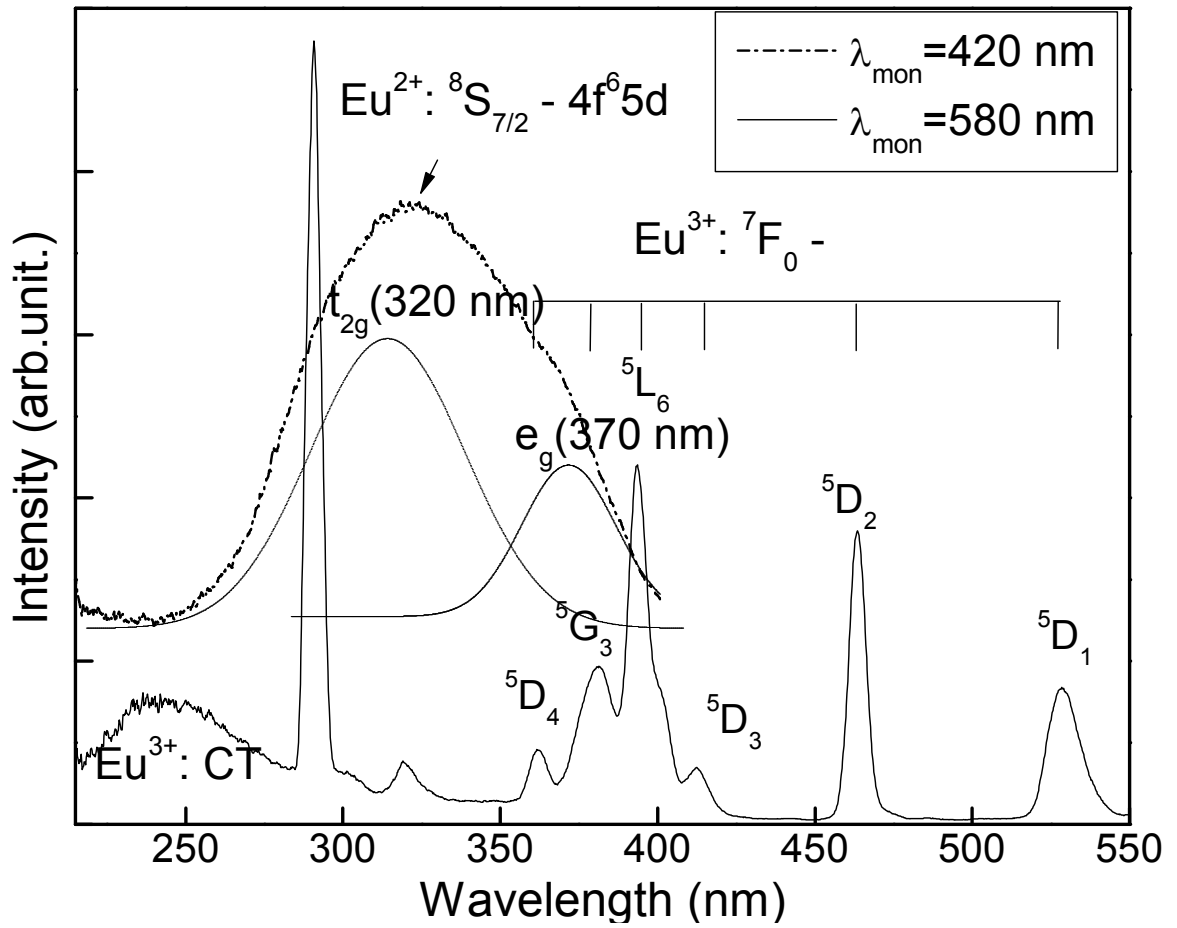


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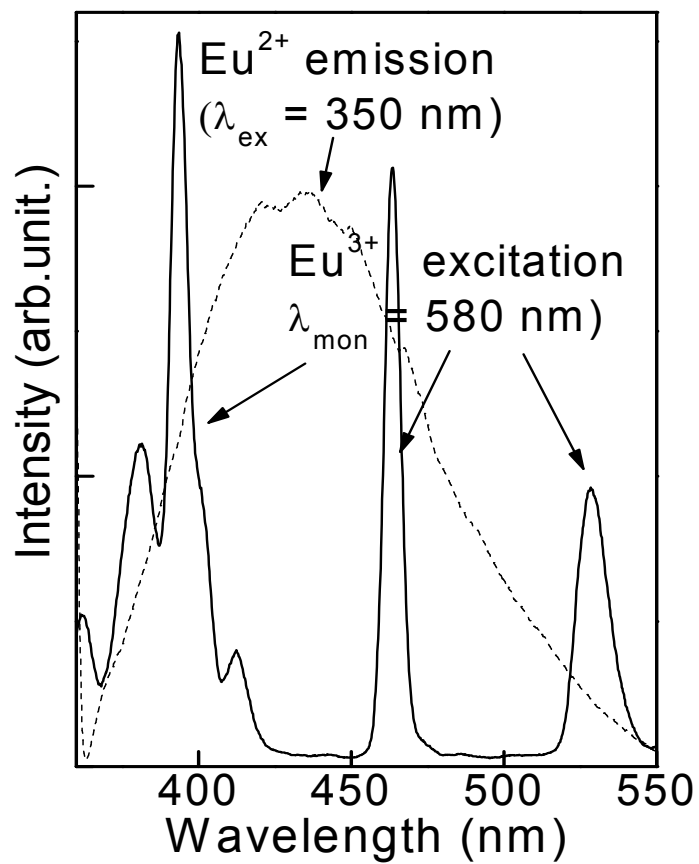


Figure 4.

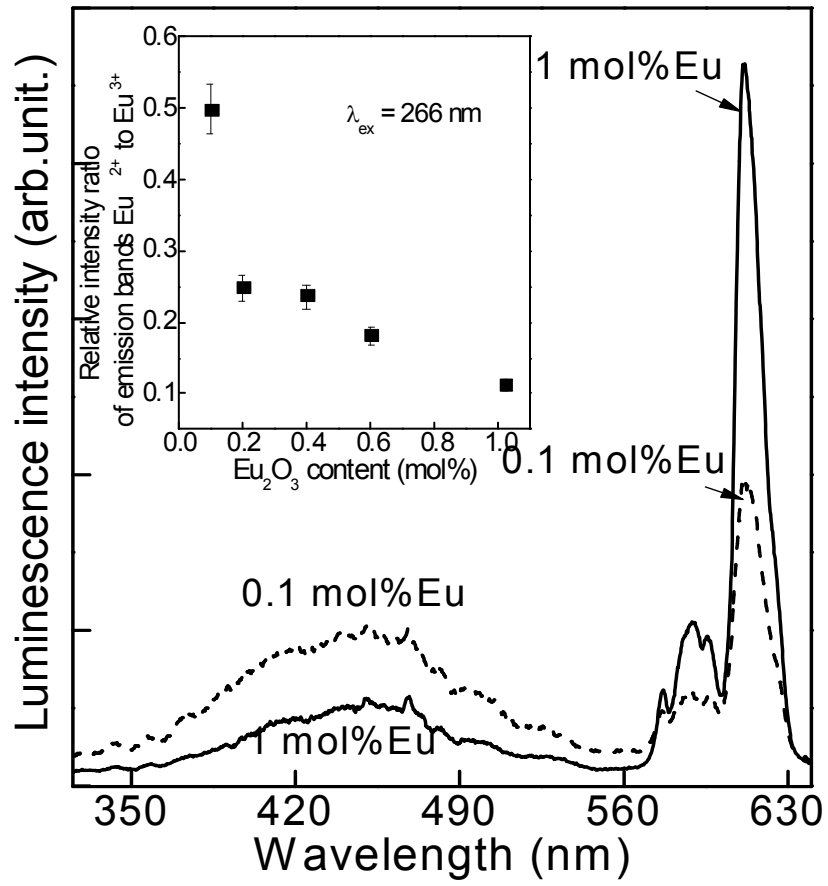


Figure 5.

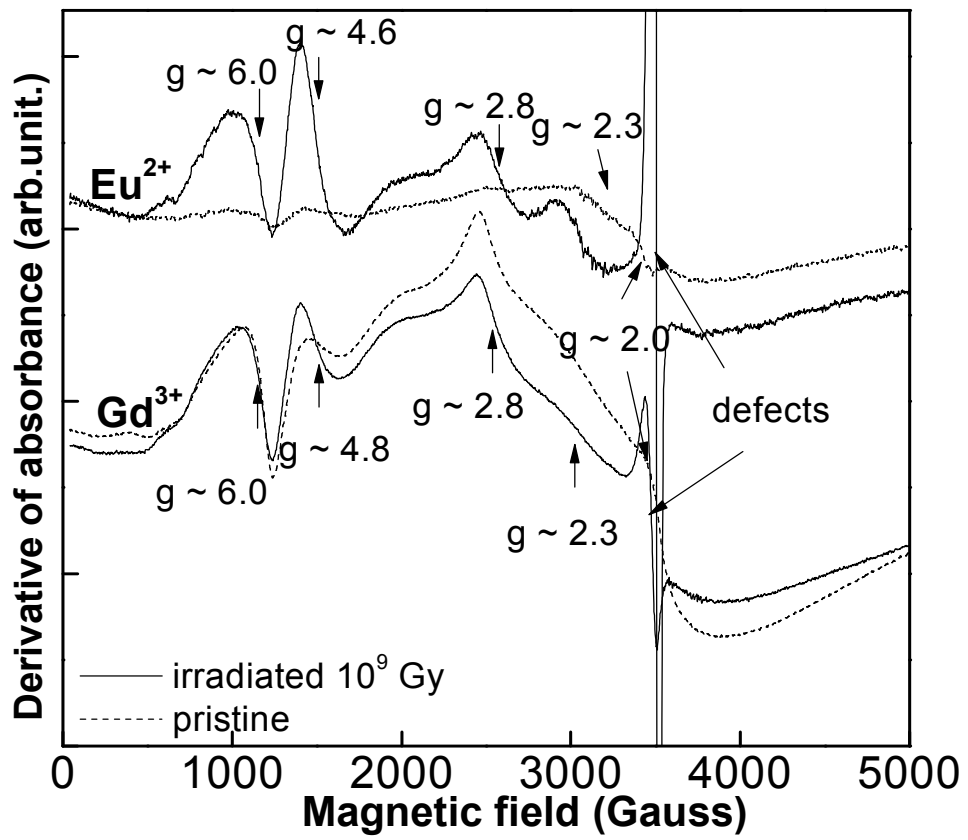


Figure 6.

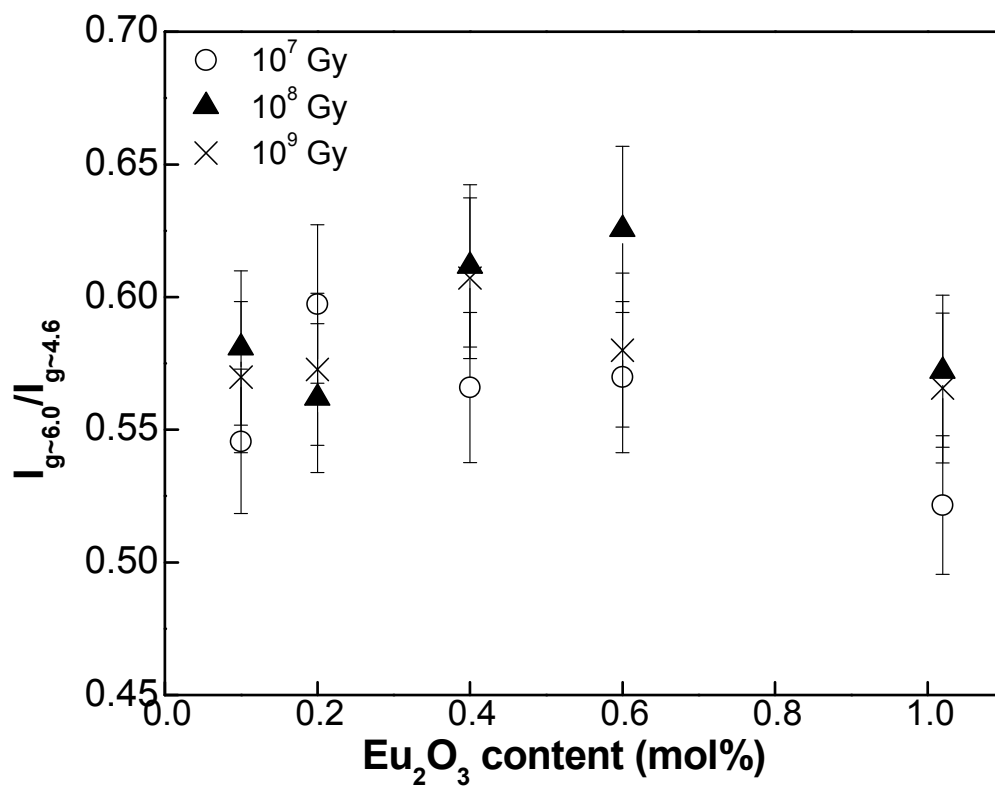


Figure 7.

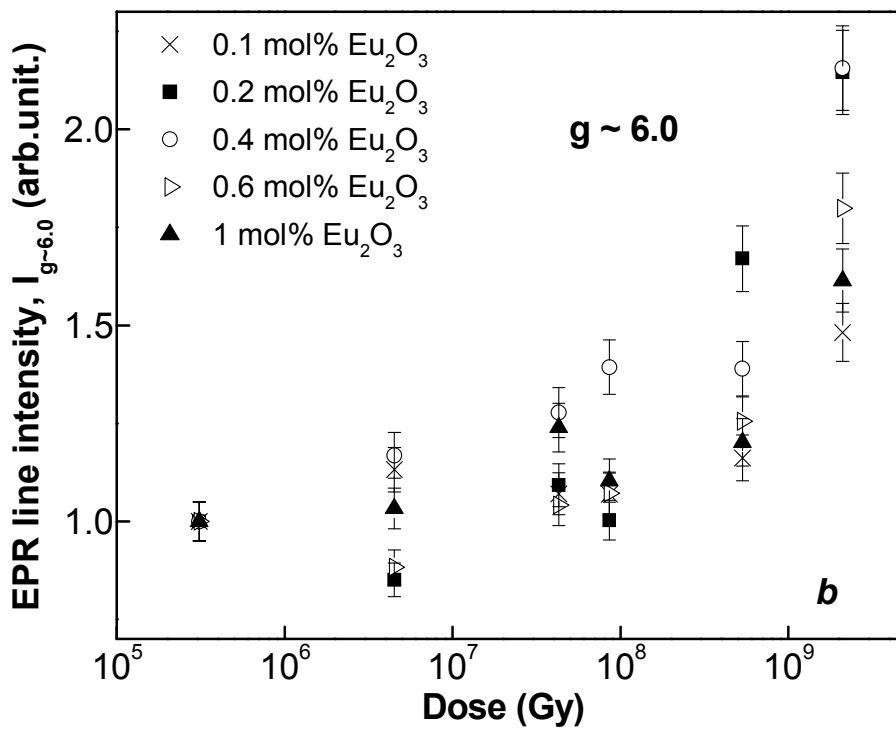
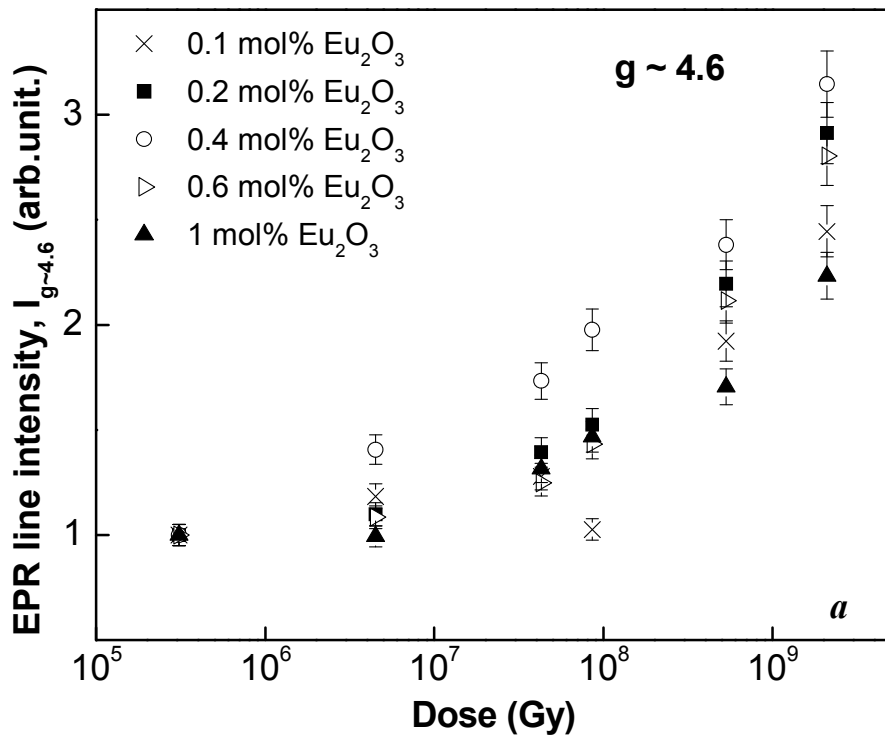




Figure 8.

