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

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Abstract

Eu_2O_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 Eu^{3+} and 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 Eu_2O_3 concentration leads to the increase of Eu^{3+} luminescence intensity while the luminescence intensity of Eu^{2+} ions tends to reduce. Although as it is seen by Electron Paramagnetic Resonance spectroscopy amount of Eu^{2+} ions inside the glass is raised with total Eu_2O_3 concentration. The difference in the results of both spectroscopies is explained in terms of energy transfer from Eu^{2+} to Eu^{3+} leading to an Eu^{2+} luminescence quenching. Irradiation results in the increase of reduced Eu^{2+} quantity detected by Electron Paramagnetic Resonance measurements. It was shown that 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 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 β -irradiation in order to simulate the consequences of β -decay and predict influence RE ions on structure of host matrices [4-6]. Europium is representative of actinides as the chemical properties of Eu^{3+} are very similar to those of trivalent actinides and in particular to Am^{3+} . Furthermore, Eu^{3+} can be used as a local structural probe with different spectroscopic methods [7,8].

The coexistence of both Eu^{3+} and 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 H_2 or CO , is generally needed to reduce Eu^{3+} to Eu^{2+} during the synthesis of Eu^{2+} doped luminescent materials. However, the preparation of Eu^{2+} doped materials in air is more convenient than in reducing atmosphere. Some research works on reduction of Eu^{3+} into 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 Eu^{3+} ion is an active electron trap [18], it is apparent to consider that ionizing radiation such as γ -rays [18-21] or irradiation with femtosecond laser

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

In continuation of our recent studies, we investigated Eu^{3+} reduction process in pristine and exposed to β -irradiation ABS glasses doped with Eu_2O_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 % SiO_2 , 4.00 % Al_2O_3 , 22.41 % B_2O_3 , 12.12 % Na_2O , 1.70 % ZrO_2 . Eu-doped ABS glasses were prepared by adding to the base glass different amounts of **europium oxide Eu_2O_3** (from 0.1 to 1 mol%). The dried mixed powders were first heated at 750°C in a Pt crucible during 10 hours for removing carbonate from the reagents. Then, it was melted at 1500°C for one hour and quenched in air. The different glasses were annealed at 500°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 β -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 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 Eu_2O_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 Eu^{3+} [15,17]. Appearance of the broad band positioned between 350-500 nm can be assigned to the 5d - 4f transition of Eu^{2+} ions [15,17]. The observed emission bands under different wavelength of excitation are basically the same but the contribution of both Eu^{3+} and Eu^{2+} emission intensity is different. It can be seen from **Fig. 1** that excitation in the Eu^{2+} band (330 and 350 nm) results in the higher luminescence intensity of Eu^{2+} ions while Eu^{3+} ions luminescence is negligible. Indeed, 5d band of 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 Eu^{2+} ions. At the same time a weak band at 320 nm can also be distinguished in the Eu^{3+} excitation spectrum, indicating the presence of energy transfer (**ET**) from Eu^{2+} ions 5d level to the Eu^{3+} ions 4f levels. It is apparent from Fig. 3, that the overlap between broad emission of Eu^{2+} and the different excitation bands of Eu^{3+} can result in energy transfer from Eu^{2+} to Eu^{3+} ions increasing the Eu^{3+} emission efficiency. Indeed, as it can be seen from **Fig. 4**, the increase of Eu_2O_3 content into the ABS glass leads

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

Additional evidence of 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% Eu_2O_3 doped ABS glasses. It is known that Eu^{3+} ion is not paramagnetic one and therefore does not make contribution in EPR signal. By contrary, 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 Eu^{2+} ion has the same electronic configuration as Gd^{3+} ion and, as expected, EPR spectra of Eu^{2+} -doped ABS glasses are similar to those of 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 $g \sim 6.0$ (~ 1154 G), $g \sim 2.8$ (~ 2570 G) and 2.0 (~ 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 Eu^{2+} doped glasses comparing to Gd^{3+} -doped glass. Besides, the relative proportion between intensities of EPR line at $g \sim 4.6$ (~ 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 $g \sim 2.3$ (~ 3060 G) is found to be correlated to some paramagnetic impurity.

It should be noted that quantity of reduced Eu^{2+} ions is affected by the Eu concentration. It is apparent, that with the increase of Eu_2O_3 content in ABS glasses, the

intensity of EPR lines associated with Eu^{2+} ions increases, although relative ratio between two Eu^{2+} bands ($g \sim 4.6$ and 6.0) reveals negligible dependence with doping ion concentration (**Fig. 6**). The evolution of observed 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 $g \sim 2.0$ (~ 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 Eu_2O_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 (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 Eu^{3+} and 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 Eu^{2+} ion. Intensity of Eu^{2+} ions is increased while the intensity of Eu^{3+} drastically decreases with changing of wavelength of excitation **which is apparently related to the fact that the Eu^{2+} excitation band is a broad one while 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 O_2^- to 4f levels

of 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 Eu^{2+} ion is observed as it is shown in Fig.2. The 4f – 5d excitation band of 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 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 (~ 370 nm) indicates that the 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 Eu^{3+} can be ascribed to 4f-5d transition of Eu^{2+} . Moreover strong overlap between broad blue emission of Eu^{2+} and excitation bands of 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 Eu^{2+} and Eu^{3+} ions [31] it is possible to suppose that energy transfer from Eu^{2+} to 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 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 Eu^{3+} ion.** We also observed another evidence of energy transfer from Eu^{2+} ions to Eu^{3+} by measuring the relative ratio between emission intensities for both ions (Fig.4). Indeed, diminution of Eu^{2+} emission intensity with simultaneous enhancement of Eu^{3+} luminescence as a function of Eu_2O_3 concentration is caused by non-radiative relaxation of Eu^{2+} ion to the ground state (${}^8S_{7/2}$) providing energy transfer (resonant or through re-absorption [33]) to Eu^{3+} ions.

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

broadening of the 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 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 Eu^{2+} ions.

Since Eu^{2+} ion is equivalent for EPR to 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 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 Gd^{3+} ions in one site. On the contrary, EPR signal at $g \sim 4.8$ is corresponding to a Gd^{3+} site different from the one observed in the “U”-spectrum [36,42,43]. Indeed, our recent study of irradiated 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 Gd^{3+} environments in the glass investigated [4].

However, it was underlined in [29] that Eu^{2+} and 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 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 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 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 Eu^{2+} is attributed to a network modifiers location for the Eu^{2+} ion.

Amount of defects created under irradiation is decreased by the increase of Eu_2O_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 β -irradiated aluminoborosilicate glasses doped with Sm^{3+} or 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 Gd^{3+} ions considered as an analogue to 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 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 Eu_2O_3 concentration one can see the decrease of relative proportion between hole (BOHC) and electron (E') defects in dependence on Eu_2O_3 concentration. It is well-known that 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 Eu_2O_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 Eu^{3+} and Eu^{2+} ions can coexist simultaneously in the as-prepared glass. Luminescence properties of Eu^{2+} ions are found to be concentration-dependent. Energy transfer between Eu^{2+} and Eu^{3+} ions is assumed to be responsible for the Eu^{2+} emission quenching and enhancement of Eu^{3+} luminescence efficiency. At the same time Electron Paramagnetic Resonance measurements confirm the strong increase of the Eu^{2+} ions quantity in aluminoborosilicate glasses with increase of Eu_2O_3 concentration as well as with irradiation dose. Moreover, observed Electron Paramagnetic Resonances let us suppose that the position of 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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References

- [1] A.Haddi, F.Farges, P.Trocellier, E.Curti, M.Harfouche, G.E.Brown. Proceedings of 13th Conference on X-Ray Absorption Fine Structure (XAFS13), July 9-14, 2006 Stanford California.
- [2] C. Lopez, X. Deschanel, J.M. Bart, J.M. Boubals, C. den Auwer, E. Simoni. *J.Nucl. Mater.* 312 (2003) 76.
- [3] P.Loiseau, D.Cauran, N.Baffier, L.Mazerolles, C.Fillet. *J. Nucl. Mater.* 335 (2004) 14.
- [4] E. Malchukova, B. Boizot, D. Ghaleb, G. Petite. *J. Non-Cryst.Solids* 352 (2006) 297.
- [5] E. Malchukova, B. Boizot, G. Petite, D. Ghaleb, *J. Non-Cryst. Solids* 353 (2007) 2397.
- [6] E. Malchukova, B. Boizot, G. Petite, D. Ghaleb, *Eur.Phys.J.Appl.Phys.*45 (2009) 10701.
- [7] N. Ollier, G. Panczer, B. Champagnon, G. Boulon, P.Jollivet, *J. Lumin.* 94&95 (2001) 197.
- [8] F. Thevenet, G. Panczer, P. Jollivet, B. Champagnon, *J. Non-Cryst. Solids* 351 (2005) 673.
- [9] Z. Lian, J. Wang, Y.H. Lv, S.B. Wang, Q. Su, *J. Alloys Compd.* 430 (2007) 257.
- [10] J.H. Hao, J. Gao, *Appl. Phys. Lett.* 85 (2004) 3720.
- [11] J.H. Hao, J. Gao, M. Cocivera, *Appl. Phys. Lett.* 82 (2003) 2778.
- [12] M.Y. Peng, Z.W. Pei, G.Y. Hong, Q. Su, *Chem. Phys. Lett.* 371 (2003) 1.
- [13] H.P. Xia, J.L. Zhang, J.H. Wang, Q.H. Nie, H.W. Song, *Mater. Lett.* 53 (2002) 273.
- [14] Z.W. Pei, Q.H. Zeng, Q. Su, *J.Phys. Chem. Solids* 61 (2000) 9.
- [15] M. Nogami, T. Kawaguchi, A. Yasumori, *Opt. Commun.* 193 (2001) 237.
- [16] C. Wang, M.Y. Peng, N. Jiang, X.W. Jiang, C.J. Zhao, J.R. Qiu, *Mater. Lett.* 61 (2007) 3608.
- [17] S. Liu, G. Zhao, W. Ruan, Z. Yao, T. Xie, J. Jin, H. Ying, J. Wang, G. Hanw. *J. Am. Ceram. Soc.*, 91 (2008) 2740.
- [18] R.Yokota. *J.Phys.Soc.Japan* 23 (1967) 129.

- [19] V.I. Arbuzov, M.N. Tolstoj, M.A. Elerts. *Fizika i Khimiya Stekla. (Glass Physics and Chemistry)* 11 (1985) 547.
- [20] V.I. Arbuzov, M.N. Tolstoj, M.A. Elerts, Ya.S. Trokshs. *Fizika i Khimiya Stekla (Glass Physics and Chemistry)* 13 (1987) 581.
- [21] A.Shida, S.T.Yakamuku. *Chem. Lett.* 9 (1988) 1497.
- [22] J. Qiu, K. Kojima, K. Miura, T. Mitsuyu, K. Hirao, *Opt. Lett.* 24 (1999) 786.
- [23] H. You, M. Nogami. *J.Phys.Chem.B* 109 (2005) 13980.
- [24] Q. H. Zeng, Z. W. Pei, S. B. Wang, Q. Su. *J. Alloys Compd.* 275–277 (1998) 238.
- [25] C. Zhu, Y. Yang, X. Liang, S. Yuan, G. Chen. *J. Am. Ceram. Soc.*, 90 (2007) 2984.
- [26] S Schweizer, G Corradi, A Edgar and J-M Spaeth. *J. Phys.: Condens. Matter* 13 (2001) 2331.
- [27] B. Boizot, G. Petite, D. Ghaleb, and G. Calas, *Nucl. Instr. and Meth. in Phys. Res. B* 141 (1998) 580.
- [28] H. Liang, Q. Zeng, Y. Tao, S. Wang, Q. Su, *Mater. Sci. Eng. B* 98 (2003) 213.
- [29] H. Ebendor-Heidepriem, D. Ehrt. *Opt.Mater.* 15 (2000) 7.
- [30] M. Nogami, Y. Abe. *Appl. Phys. Lett.* 69 (1996) 3776.
- [31] M. Nogami, T. Yamazaki, Y. Abe. *J. Lumin.* 78 (1998) 63.
- [32] K.-S. Lima, S. Lee, M.-T. Trinh, S.-H. Kim, M. Lee, D. S. Hamilton, G. N. Gibson. *J. Lumin.* 122–123 (2007) 14.
- [33] D. Zhou, R.Y. Chen, C. Shi, Y. Wei, H. Chen, M. Yin, *J. Alloy. Compd.* 322 (2001) 298.
- [34] I. Ardelean, E. Burzo, D. Mitulescu-Ungur, S. Simon, *J. Non-Cryst.Solids* 146 (1992) 256.
- [35] E. Culea, I. Milea, *J. Non-Cryst. Solids* 189 (1995) 246.
- [36] S. Simon, I. Ardelean, S. Filip, I. Bratu, I. Cosma, *Solid State Commun.* 116 (2000) 83.
- [37] E. Culea, L. Pop, S. Simon, *Mater. Sci. Eng. B* 112 (2004) 59.

- [38] D.L. Griscom, *J. Non-Cryst. Solids* 40 (1980) 211.
- [39] I.E. Iton, C.M. Brodbeck, S.L. Suib, G.D. Stucky, *J. Chem. Phys.* 79 (1983) 1185;.
- [40] C.M. Brodbeck, I.E. Iton, *J. Chem. Phys.* 83 (1985) 4285.
- [41] C. Legein , J .Y.Buzare , G. Silly, C. Jacoboni. *J. Phys.: Condens. Matter* 8 (1996) 4339.
- [42] E. Culea, A. Pop, I. Cosma. *J. Magnet.* 157/158 (1996) 163.
- [43] I. Ardelean, L. Griguta. *J.Non-Cryst. Solids* 353 (2007) 2363.
- [44] C.B. Azzoni, D. Di Martino, A. Paleari, A. Speghini, M. Bettinelli. . *J.Mater.Sci.* 34 (1999) 3931.
- [45] D. Furnisst, E. A. Harrist, D. B. Hollis. *J. Phys. C: Solid State Phys.* 20 (1987) L147.
- [46] J. M. D. Coey, A. McEvoy, M.W. Shafer. *J. Non-Cryst. Solids* 43 (1981) 381.
- [47] E. Malchukova, B. Boizot, G. Petite, D. Ghaleb. *J. Non-Cryst Solids* 354 (2008) 3592.
- [48] J. de Bonfils, G. Panczer, D. de Ligny, S. Peugot, B. Champagnon. *J.Nucl. Mater.* 362 (2007) 480.

Figure Captions

Figure 1: Luminescence spectra of pristine as-prepared Eu-doped ABS glass (0.2 mol% of Eu_2O_3) in dependence on excitation wavelength (Xe lamp)

Figure 2: Excitation spectra for Eu^{2+} and Eu^{3+} ions monitored at 420 and 580 nm, respectively, measured for pristine as-prepared Eu-doped ABS glass (0.2 mol% of Eu_2O_3)

Figure 3: Overlap of Eu^{2+} luminescence spectrum (**350 nm**) with Eu^{3+} excitation spectrum of pristine as-prepared Eu-doped ABS glass (**580 nm**) (0.2 mol% of Eu_2O_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 Eu_2O_3 concentration; in inset – the intensity ratio $\text{Eu}^{2+}/\text{Eu}^{3+}$ as a function of Eu_2O_3 content**

Figure 5: EPR spectra of pristine and irradiated Eu- and Gd-doped ABS glass (0.6 and 0.57 mol% of Eu_2O_3 and Gd_2O_3 , respectively)

Figure 6: **Ratio between EPR line intensities** at $g \sim 4.6$ and $g \sim 6.0$ as a function of Eu_2O_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 Eu_2O_3 concentration in β -irradiated glasses ($5.3 \cdot 10^8$ Gy); **in inset – radiation defect content as a function of Eu_2O_3 concentration**

Figure 1

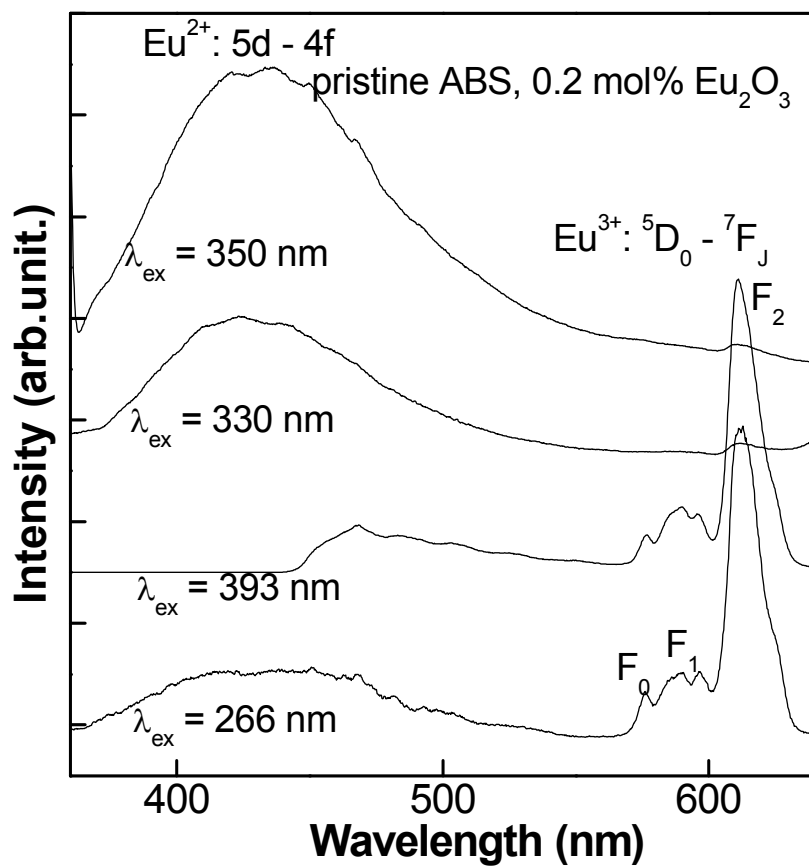


Figure 2.

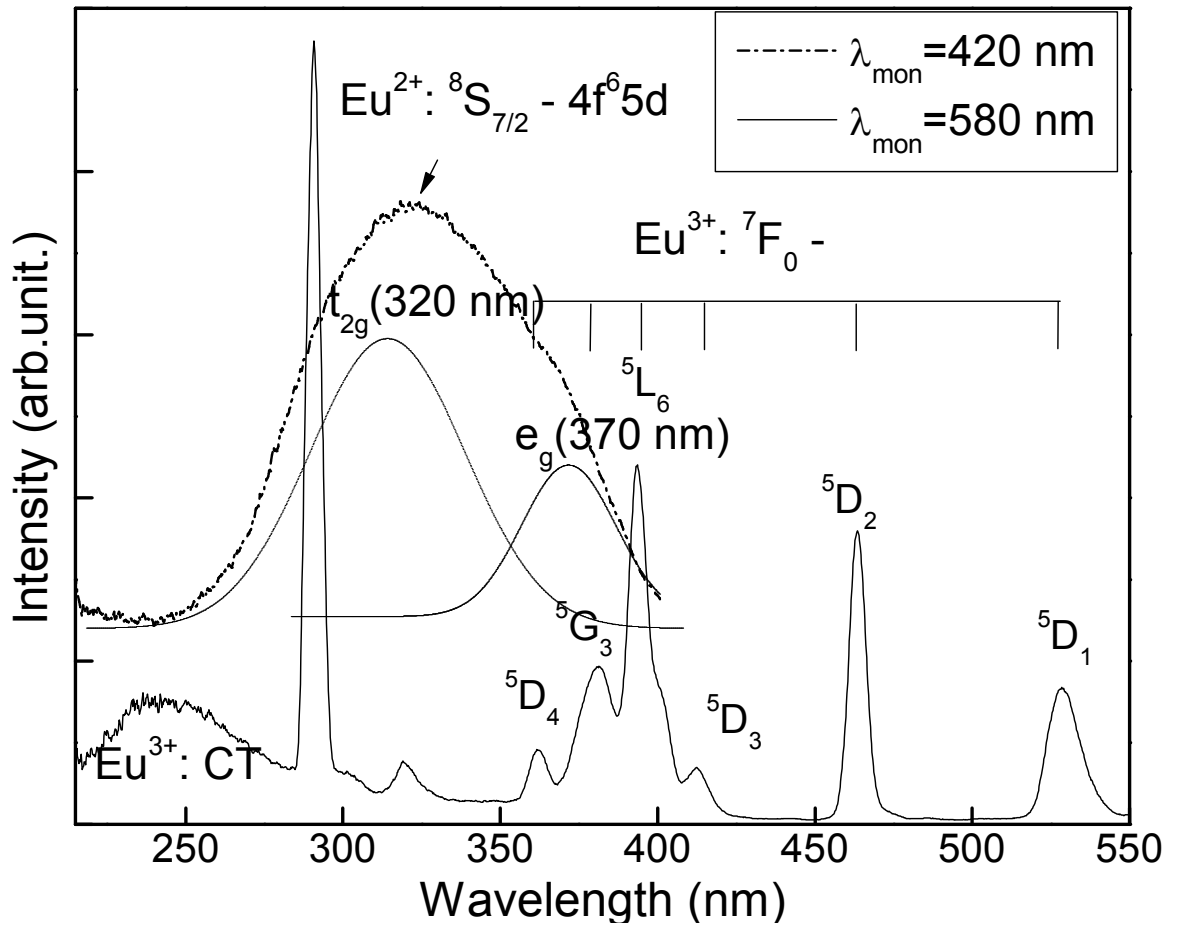


Figure 3.

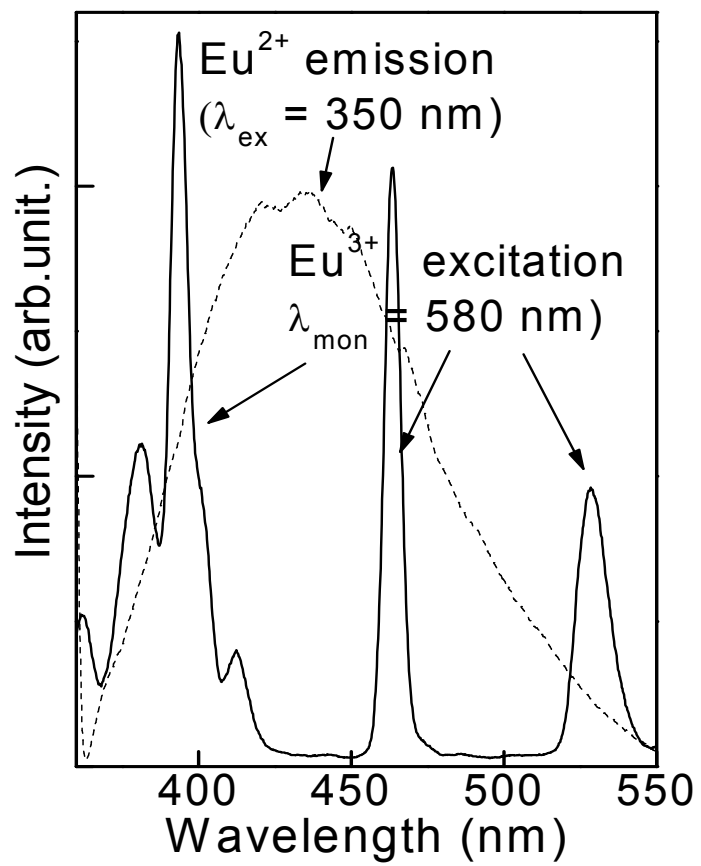


Figure 4.

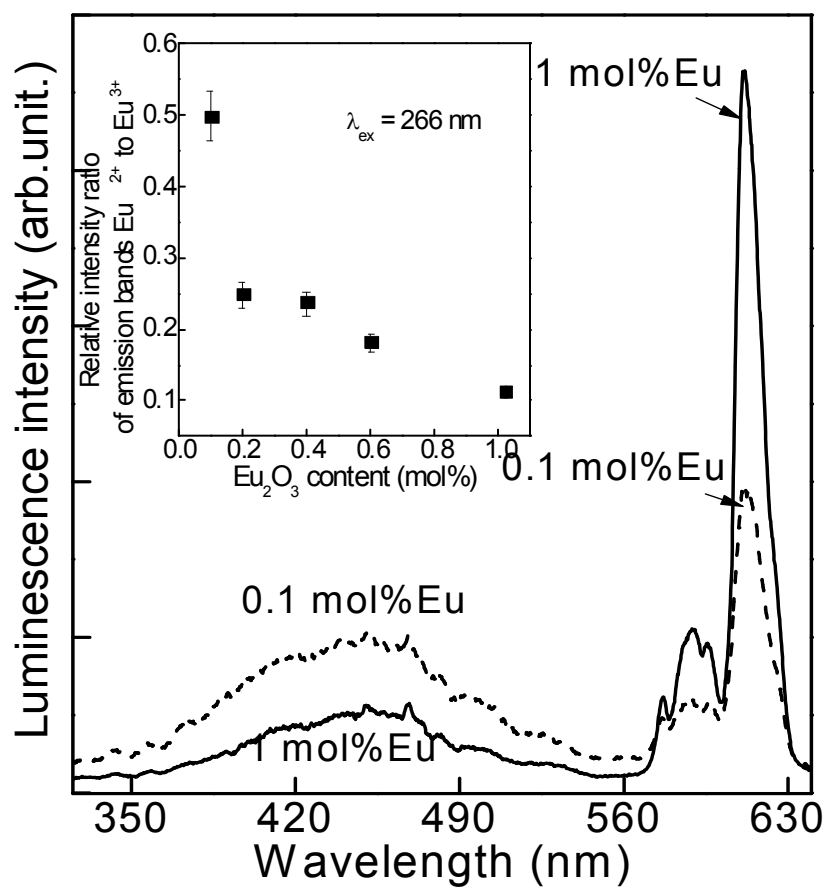


Figure 5.

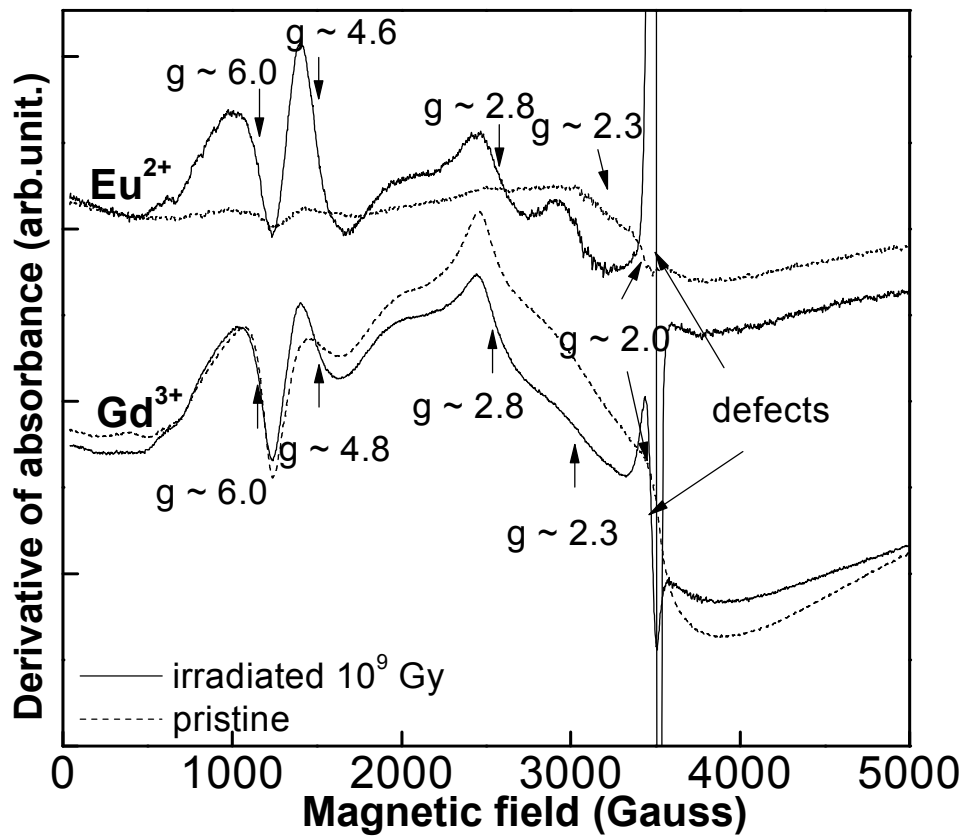


Figure 6.

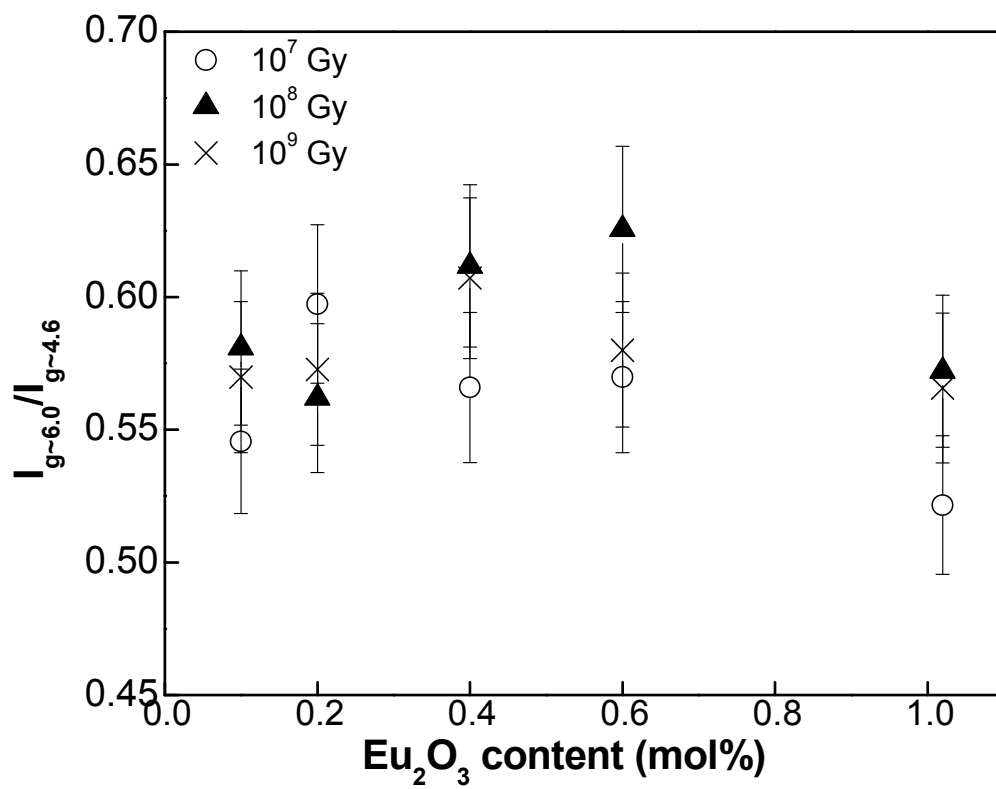


Figure 7.

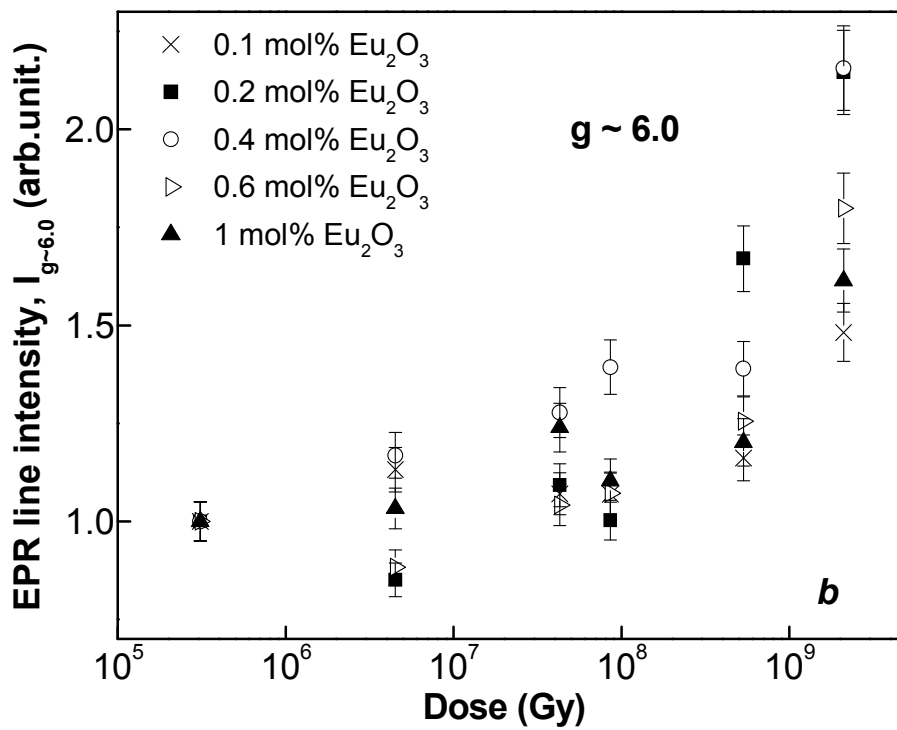
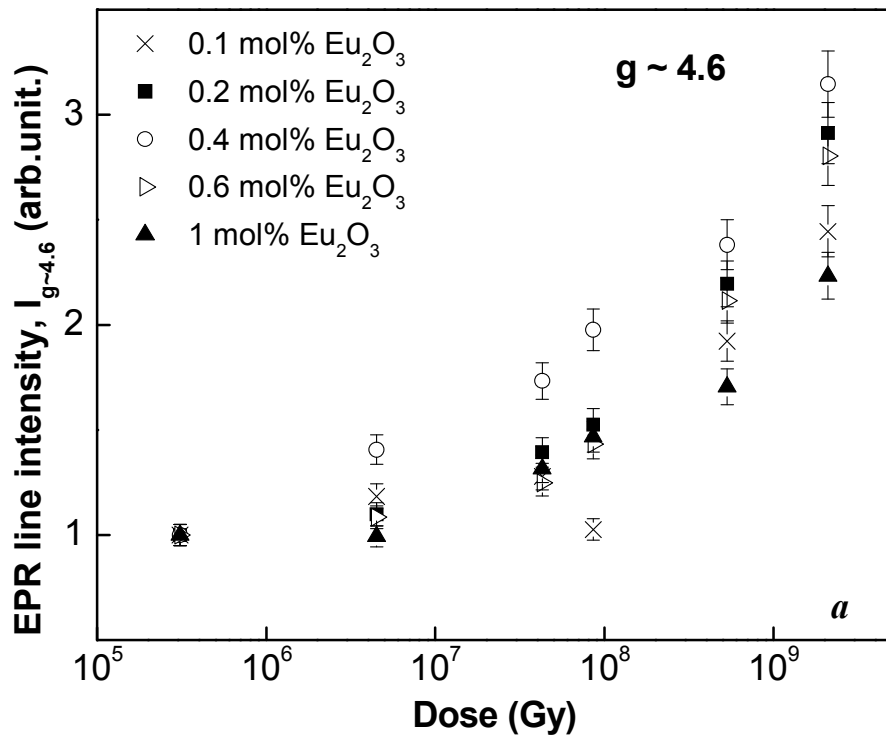


Figure 8.

