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► **To cite this version:**

Mohamed Mahfoudhi, Nadège Ollier. Tuning Eu^{2+} amount and site symmetry in phosphate glasses under irradiation by electron energy and integrated dose. *Optical Materials*, 2019, 95, pp.109253 -. 10.1016/j.optmat.2019.109253 . hal-03487287

HAL Id: hal-03487287

<https://hal.science/hal-03487287v1>

Submitted on 20 Dec 2021

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Tuning Eu²⁺ amount and site symmetry in phosphate glasses under irradiation by electron energy and integrated dose

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Abstract:

This paper relates the formation of Eu²⁺ under 700 keV and 2.5 MeV irradiation in meta and polyphosphate glasses. EPR and photoluminescence measurements evidenced the presence of two sites for Eu²⁺ ions corresponding to low-symmetry and high-symmetry sites. We highlighted that the glass composition and in particular the presence of **ZnO** favors the formation of high-symmetry sites. Moreover, we found out that 700 keV electron energy is much more efficient to produce Eu²⁺ ions compared to 2.5 MeV. This is probably linked to an enhancement of the alkaline migration generated under the charge depletion induced by the 700 keV electrons implantation. This migration depolymerizes the network structure and tends to favor the formation of Eu²⁺. The same tendency is observed at 2.5 MeV when the dose is higher than 1 GGy.

Introduction

Phosphate glasses are known as suitable matrix to incorporate large amount of Rare Earth Element (REE) and limiting clustering effect contrary to silica. P atoms in silica fibers were also proved to be powerful in the Yb cluster dissolution [1]. Moreover, their low T_g (lower than 450°C) makes them interesting for industrial applications such as optics, biomedicine, data storage and energy applications [2-8]. Rare earth element doped glasses are commonly used in optics as amplifier, laser materials...

Many recent papers [10–13] show the interest of Eu-doped glasses (aluminosilicate, fluoro-aluminoborate, tellurite, lead phosphate) for phosphors and luminophore applications.

Eu^{2+} is one of the REE used in phosphor materials by emitting light in a broad blue range due to $4f \rightarrow 5d$ transitions, while Eu^{3+} ions exhibit lines narrower in the red range.

From the applicative point of view, it can be very attractive to adjust the emission spectra of Eu-doped phosphors by modifying $\text{Eu}^{2+}/\text{Eu}^{3+}$ relative concentration and site symmetry of each valence state. Different solutions exist to reach this goal: the first one is to produce glasses under reduced atmosphere that mostly affects the $\text{Eu}^{2+}/\text{Eu}^{3+}$ ratio. Some papers report a heat treatment or play on the glass composition to reduce the Eu^{3+} into Eu^{2+} ions. As an example, Bouchouicha et al. [13] investigated the luminescence properties of Eu^{2+} ions in calcium aluminosilicate glass-ceramics after annealing and they reported a remarkable increase of the emission intensity and a shift towards lower wavelength with increasing time-heat treatment. This phenomenon is interpreted by the incorporation of Eu^{2+} ions into crystalline phases after the reduction of Eu^{3+} ions.

The second one resides on the use of irradiation. The reduction of Eu^{3+} into divalent Eu^{2+} was demonstrated in literature by using electrons in borosilicate by Mougnaud et al. [14] and in aluminoborosilicate glasses by Malchukova et al. [15] or by UV laser and X-ray by Ehrt et al. [16,17] in phosphate. Furthermore, the reduction of the Eu^{3+} to Eu^{2+} ions under femtosecond laser irradiation has been also observed in aluminoborosilicate glasses [18] or borate glasses [19]. Qiu et al.[20] were the first to evidence electron trapping on Eu^{3+} under fs laser in fluorozirconate type glass. We also evidenced strong modification of the Eu^{3+} site symmetry depending on the dose and glass composition in agreement with the few works in literature that reported a Eu^{3+} ions environment variation under electron in oxyfluoride glass [21] and in borosilicate glasses under gamma [22] and gold ion irradiation [23]. Our results will be published in a coming article.

In the present study, we will show how it is possible to impact both the site symmetry and the amount of produced Eu^{2+} by optimizing the electron energy (700 keV vs 2.5 MeV) and the integrated dose from 10^5 to 4×10^9 Gy in phosphate glass types (metaphosphate and polyphosphate). The site dependence versus the nature of the glass additionally will be also analyzed.

Experimental part:

Various undoped and Eu-doped phosphate glasses were prepared by the standard melt-quenching method. Appropriate amounts of $(\text{NH}_4)_2\text{HPO}_4$, Na_2CO_3 , Li_2CO_3 , K_2CO_3 , MgO , ZnO and Eu_2O_3 were mixed and melted slowly in silica crucible up to 900-1200°C depending on the composition using electric muffle furnace. The melted glass was quenched rapidly into

Pt-Au crucible at 230°C and then annealed immediately at 270°C to release residual internal strains.

The nominal glass composition is presented in table 1.

The glass samples were irradiated by SIRIUS electron accelerator (Laboratoire des Solides Irradiés, Palaiseau, France) with 2.5 MeV electron beam at various doses from 10^5 Gy to 4.15×10^9 Gy and with 700 keV electrons at 10^8 and 10^9 Gy. With 2.5 MeV electrons, the whole sample volume (4x4x0.8mm) was homogeneously irradiated contrary to 700 keV energy where electrons are stopped in the glass at 600 μ m depth (sample thickness \sim 1.2 mm).

Time-resolved photoluminescence (PL) spectra were recorded using Shamrock SR-303i spectrometer related to an ANDOR ICCD camera. 532, 355 and 266 nm laser excitations (pulsed Nd: YAG INDI laser) were used.

The electron paramagnetic resonance (EPR) spectra were carried out with Bruker X-band EMX spectrometer at 9.8 GHz frequency. All measurements were performed at room temperature and the derivative signals obtained are normalized by mass sample and gain.

Results:

A zoom of the time-resolved photoluminescence emission spectra under 355 nm excitation in the 400-525 nm range is exhibited in Figures 1a and 1b. They correspond respectively to metaphosphate glass (Meta-Na-Eu) and polyphosphate glass (Poly-Zn-Na-Eu) irradiated by electrons of 2.5 MeV at various doses from 10^5 Gy to 4.15×10^9 Gy (delay = 200 ns and gate width = 30 μ s). It seems that the large emission band at 460 nm increases with dose in metaphosphate glasses (Fig 1a) while the emission spectra in polyphosphate glasses show a new narrow band between 400 and 450 nm. The intensity of this band tends to decrease with dose as shown in Fig. 1b. Nevertheless, a large band centered at 490 nm is visible on those spectra.

Fig 2a and 2b compare the emission spectra of Meta-Na-Eu and Poly-Zn-Na-Eu irradiated by electrons of 700 keV and 2.5 MeV respectively at similar doses 10^8 and 10^9 Gy. Fig 2a shows that the intensity of the emission band centered at 450 nm and attributed to Eu^{2+} ion is strongly increased after 700 keV electron irradiation compared to 2.5 MeV energy. Moreover, a red shift of the broad emission band occurs when the dose increases from 10^8 to 10^9 Gy for 700 keV electrons in Na metaphosphate glass. This emission shape variation could be explained by the existence of two different Eu^{2+} sites and the ratio between both sites depending on the dose. **A careful fit of each emission spectra was performed, the results obtained for metaphosphate and polyphosphate at 700 keV and 10^9 Gy are shown in Figure 3. We observed 2 components at 450 and 500 nm in both glasses attesting the presence of 2 sites for Eu^{2+} ions.**

Fig 2b displays as well a strong increase of the 500 nm band intensity after 700 keV electron irradiation compared to 2.5 MeV in polyphosphate glass. Electronic paramagnetic resonance (EPR) spectroscopy is a powerful tool to obtain complementary quantitative data on Eu^{2+} formation under irradiation (indeed Eu^{2+} is a $4f^7$ paramagnetic ion). Fig. 4 displays the EPR spectra of Poly-Zn-Na-Eu glasses before and after 2.5 MeV irradiation for various doses.

After irradiation, new signals at 1095 G ($g = 6.3$), 2466 G ($g=2.8$) and 3500 G ($g=2.0$) can be observed. These components are known as the “U” EPR signal and can be attributed to Eu^{2+} ions associated to a low-symmetry site whereas the signal at 1492 Gauss ($g = 4.7$) corresponds to a high-symmetry site of divalent europium [12]. We can observe at $g = 2$ a sharp saturated line that corresponds to the P-related point defects such as POHC (Phosphorus Oxygen Hole Centers). The detailed nature of point defects associated to P will not be described here. Furthermore, we can notice that all the signals associated to Eu^{2+} directly correlated to the Eu^{2+} amount increases with the irradiation dose.

Fig 5a and 5b report the peak to peak intensity of the EPR signals at $g = 6.3$ and $g = 4.7$ of Meta-Na-Eu, Meta-Zn-Eu, Poly-Zn-Na-Eu and Poly-Zn-Na-Eu($\text{Q}^1/\text{Q}^2:50/50$) corresponding to low and high symmetry sites of Eu^{2+} respectively as a function of the dose logarithm. We observe in fig 5a and 5b that both signals are weak and constant regardless of the dose in Meta-Na-Eu glass. In contrast, in presence of zinc oxide in the glasses, a quasi-linear increase of both lines at $g= 6.3$ and $g = 4.7$ occurs with the dose logarithm. The formation of Eu^{2+} is more efficient in Poly-Zn-Na-Eu ($\text{Q}^1/\text{Q}^2:50/50$) than in Poly-Zn-Na-Eu, while meta-Zn-Eu and Poly-Zn-Na-Eu exhibits quite similar efficiency of Eu^{3+} reduction under irradiation. Moreover, it can be notice that a lowest amount of Eu^{2+} is formed under the high-symmetry site.

In Figure 6, the intensity of $I_{g=6.3}$ signal corresponding to the low-symmetry Eu^{2+} site (Fig. 6a) and $I_{g=4.7}$ to the high-symmetry site (Fig. 6b) are reported for all glasses. It allows to compare the Eu^{3+} reduction efficiency between 2.5 MeV (empty symbols) and 700 keV (full symbols) at 10^8 Gy and 10^9 Gy doses. We observe a huge increase of the signal intensity under 700 keV irradiation compared to 2.5 MeV and **the generation of Eu^{2+} ions is more important in polyphosphate than in metaphosphate compositions.**

$I_{g=6.3}$ (corresponding to the low symmetry site) is increased from 1 (2.5 MeV at 10^9 Gy) to 16 (700 keV, 10^9 Gy) in Meta-Na-Eu while the intensity of high symmetry sites in the same conditions is multiplied by 20. In polyphosphate glasses, a larger amount of Eu^{2+} ions is produced under 700 keV compared to metaphosphate but the **increase of Eu^{2+} reduced ions (expressed in percent) under both site symmetry shifting from 2.5 MeV to 700 keV energy is lower in Polyphosphate compared to Metaphosphate glasses. Thus, $I_{g=6.3}$ is multiplied by 8 from 700 keV to 2.5 MeV (at 10^9 Gy) (against 16 in Meta) and 11 for the signal at $g = 4.7$ (against 20 in Meta).**

In addition, it is worth to notice that a mixed alkali effect occurs in Na/K polyphosphate glass for both energies 2.5 MeV and 700 keV, especially for the high symmetry site but also for the low symmetry site within 700 keV/ 10^9 Gy conditions. Actually, a non-linear variation (with either a maximum or a minimum) of Eu^{2+} amount can be observed in Figures 6a and 6b.

Therefore, the mixed NaK zinc polyphosphate glass for the high-symmetry site exhibits the highest increase of Eu^{2+} amount from 2.5 MeV to 700 keV.

Discussion

The broad emission band around 450 nm occurring under irradiation can be attributed to the $4f^65d^1 \rightarrow 4f^7$ transition of Eu^{2+} ions. Actually, Eu^{2+} ions were detected in all irradiated

phosphate glasses whatever the dose by EPR spectroscopy. Moreover, the lifetime of the blue emission band centered at 450 nm in different glasses displays a short lifetime from 150 ns (metaphosphate) to 2.76 μ s (polyphosphate). These values are in agreement with literature examples reporting lifetimes of Eu^{2+} ions in glasses between 0.2 and 1.3 μ s in fluoride phosphate glasses Ehrt et al. [16,17].

It can be deduced from photoluminescence (fit) and EPR experiments that two different sites of Eu^{2+} coexist in electron-irradiated phosphate glasses. The presence of two types of sites for divalent Eu^{2+} ions has already been mentioned in aluminoborosilicate [9,10], aluminosilicate [25], phosphate and **fluoride-phosphate glasses** [11,12]. These studies associate generally the high symmetry site ($g=4.7$) to a strong crystal field **that could correspond to 6-coordinated Eu^{3+} ions**. The low-symmetry site ($g=6.3$) with a lower crystal field **would rather deal with Eu^{2+} ions with a higher coordination number into a modifier position**.. The shift of the $5d \rightarrow 4f$ emission band of Eu^{2+} to higher wavelengths in literature was attributed to an increase of crystal field or to a higher covalency [26]. We therefore assign the high symmetry site to the emission at 500 nm and the low-symmetry one to the emission at 450 nm. **Nevertheless, there is no clear evidence from our spectroscopic measurements that $(\text{Eu}^{3+})^-$ ions occurred from a direct trapping on two original Eu^{3+} sites already existing in the pristine glasses.**

At first, it can be seen that the glass composition and the glass polymerization impact the nature of the Eu^{2+} sites. The ratio between both sites from one composition to another one can be extracted from EPR measurements. Table 2 reports the ratio between low-symmetry site and high-symmetry site for 4 glass compositions (700 keV, 10^9 Gy). It seems that the presence of Zn favors the formation of the high-symmetry site. Figure 7 confirms the predominance of site 2 (500 nm) in polyphosphate by the red shift of the emission band. This result is supported by the table 2 where we can notice the huge intensity of the high symmetry site in polyphosphate compared to metaphosphate glasses (factor 7). This result is moreover in agreement with [26] based on the fact that polyphosphate contain more NBO than metaphosphate glasses.

However, a direct comparison of the ratio between high and low symmetry sites obtained from EPR and PL is delicate. Indeed, PL method cannot deliver absolute quantitative ratio due to two main effects: first, the photobleaching occurring under the 355 nm laser excitation inducing a decrease of the Eu^{2+} emission intensity and secondly, a mismatching between PL and EPR measurements could be due to the interaction between Eu^{2+} and other luminescent species occurring under irradiation. Additional emission bands in the 400-600 nm region were detected like the emission of diamagnetic P-defects at 410 nm [27]. This band was observed in NaMg metaphosphate glasses [28] and Na metaphosphate. The P-defect emission band in presence of Zn is not visible anymore but a new band at 435 nm (see Fig 1b) appears after irradiation. **To the best of our knowledge, such an emission band was never reported yet in irradiated phosphate glasses but we deduced that it is directly correlated to the presence of Zn. Therefore it could be attributed to unusual Zn oxidation state like Zn^+ or to $(\text{Zn}^{2+})^- \text{EC}$. $Ag=1.99$ EPR component in Zn metaphosphate glass was tentatively attributed to $(\text{Zn}^{2+})^- \text{EC}$ [29]. This EPR component at $g=1.99$ was also observed in our glasses (Meta-Zn and Poly-Zn) under 2.5 MeV and 700 keV irradiation.**

Zn doping gets a strong positive effect on the reduction efficiency of Eu^{3+} as it can be seen in Figure 4. Indeed, the comparison between the Eu^{2+} amount produced in metaZn and metaNa (up to a factor 9) supports this result. The proportion of high symmetry site is increased by increasing the amount of Zn as attested by the table 2. **This result could be explained by the fact that Zn^{2+} favors the insertion of sixfold coordinated Eu^{3+} ions in the system.** Indeed, Eu^{3+} ions can be involved in the charge compensation of Zn^{2+} under tetrahedral environment [30].

If we compare now the emission shape of Eu^{2+} in Poly-Zn-Na-Eu, Poly-Zn-K-Eu and Poly-Zn-Na-K-Eu (not shown), there is clearly no impact here of the alkali type on the $5d \rightarrow 4f$ transition position contrary to what was described by Cicconi et al. in [31] where the emission band shifts from 422 to 470 nm passing from Na to K. It can be noticed however that glasses in [31] were metaphosphate glasses and Eu^{2+} ions were reduced during the glass synthesis.

At 2.5 MeV, it seems that there is no dose effect on the ratio between site 1 and site 2. The existence of a “plateau” displayed in in Figure 8 supports this result as well as the stable shape of the photoluminescence spectra in 10^6 - 10^8 Gy range shown in figure 1. When dose becomes higher than 10^9 Gy, we can observe an increase of the ratio between both sites indicating a clear predominance of modifier sites on network modifier sites. We know from [32] that some alkali motion are involved in 2.5 MeV electron irradiated glasses when dose is higher $>10^9$ Gy. In phosphate glasses, Raman spectra of polyphosphate glasses showed some depolymerization effects for doses $>10^9$ Gy [28]. This network modification could induce a higher production of low-symmetry sites for Eu^{2+} ions. This hypothesis is supported by the nature of the low-symmetry site expected as “a modifier” site. The increase of the number of NBO under irradiation is in agreement with this scenario. The deviation from a linear behaviour visible in Fig 4 was furthermore already observed for similar doses ($>10^9$ Gy) in aluminoborosilicate glass [15].

From figure 5, by comparing same integrated dose, it is obvious to notice that 700 keV energy is much more efficient to reduce Eu^{3+} ions than 2.5 MeV. We observe in addition a real dependence on the alkali type in polyphosphate on the reduction efficiency at 700 keV and in particular the Na/Li metaphosphate and Na/K polyphosphate compositions exhibits a maximum of Eu^{2+} . **It means that the reduction of Eu^{3+} ions (specially for the high symmetry site) is probably associated to a rearrangement of the Eu^{3+} initial site including the alkaline ions and O migration in the glass network. This result let us suspect that a direct reduction process for 2 Eu^{3+} preexisting sites is probably not the right scenario but one type of Eu^{2+} ions could be generated after modification of the Eu^{3+} environment.**

We know that transport of alkaline ions is the dominant mechanism in low energy electron (typ. 50 keV) irradiated glasses with the creation of channels [33]. At 700 keV due to the thickness of the sample (larger than the penetration depth of the electrons), we expect also that migration of alkaline ions under the electrical field generated is effective. This difference with 2.5 MeV could explain the larger efficiency to reduce Eu^{3+} with low energy electrons and the ability of polyphosphate with a more depolymerized network compared to metaphosphate compositions to incorporate Eu^{2+} ions.

Conclusion

We demonstrated the high efficiency of electron irradiation to produce divalent Eu^{2+} in meta and polyphosphate ions under two types of sites. It is exacerbated under 700 keV at 10^9 Gy doses where alkaline motion is important. Moreover, the nature of the glass and the presence of Zn in the structure favors one type of site: the low symmetry sites Eu^{2+} into modifier position.

Acknowledgments

We thank EMIR program for access to SIRIUS and we appreciate O. Cavani for running electron irradiation at Ecole Polytechnique (LSI, SIRIUS, France). This work is supported by “Investissements d’Avenir” LabEx PALM (ANR-10-LABX-0039-PALM). As well, we thank G. Mountjoy for fruitful discussions of the results.

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Figures:

Figure 1 The PL emission spectra of (a) Eu-doped metaphosphate glass Meta-Na-Eu and (b) Eu-doped polyphosphate glass Poly-Zn-Na-Eu after 2.5 MeV electron irradiation at various doses from 10⁵ to over 10⁹ Gy. ($\lambda_{ext}=355$ nm)

Figure 2 The PL emission spectra of (a) Eu-doped metaphosphate glass (Meta-Na-Eu) and (b) Eu-doped polyphosphate glass (Poly-Zn-Na-Eu) after 700 keV and 2.5 MeV electron irradiation at 10^8 and 10^9 Gy doses. ($\lambda_{ext}=355$ nm)

Figure 3 A fit of the emission spectra of the Eu^{2+} ions in (a) Eu-doped metaphosphate glass (Meta-Na-Eu) and (b) Eu-doped polyphosphate glass (Poly-Zn-Na-Eu) after 700 keV electron irradiation at 10^9 Gy dose. Two components at near 450 and 500 nm in both glasses attesting the presence of 2 sites for Eu^{2+} ions.

Figure 4 EPR spectra normalized by mass and gain of Poly-Zn-Na-Eu glass irradiated by electron of 2.5 MeV at various doses.

Figure 5 Variation of the EPR signal intensity (a) $I_{g=6.3}$ and (b) $I_{g=4.7}$ attributed respectively to low and high site symmetry of Eu^{2+} ion in Meta-Na-Eu, Meta-Zn-Eu, Poly-Zn-Na-Eu and Poly-Zn-Na-Eu($Q^1/Q^2:50/50$) glasses irradiated by 2.5 MeV at various doses: from 10^5 to over 10^9 Gy

Figure 6 Comparison between 2.5 MeV and 700 keV electron irradiation of the EPR signal intensity (a) $I_{g=6.3}$ and (b) $I_{g=4.7}$ attributed respectively to low and high symmetry site of Eu^{2+} ion in meta and polyphosphate glasses for 10^8 and 10^9 Gy doses.

Figure 7 The PL emission spectra of Eu-doped meta and polyphosphate glasses (Meta-Na-Eu, Meta-Na-Mg-Eu, Meta-Zn-Eu and Poly-Zn-Na-Eu) after 700 keV at dose 10^9 Gy. ($\lambda_{ext}=355$)

Figure 8 The ratio between Eu^{2+} low-symmetry site and high-symmetry site for Poly-Zn-Na-Eu glass under 2.5 MeV irradiations as a function of dose logarithm.

Tables

Table 1 Nominal glass composition (mol%)

Table 2 Ratio between low-symmetry site and high-symmetry site for different phosphate glasses irradiated by 700 keV at 10^9 Gy dose.

Figure 1

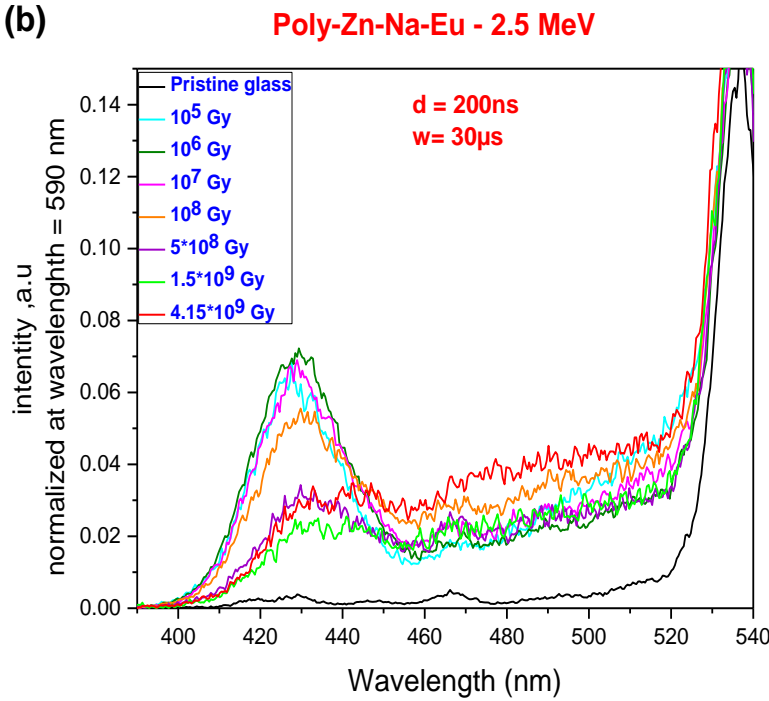
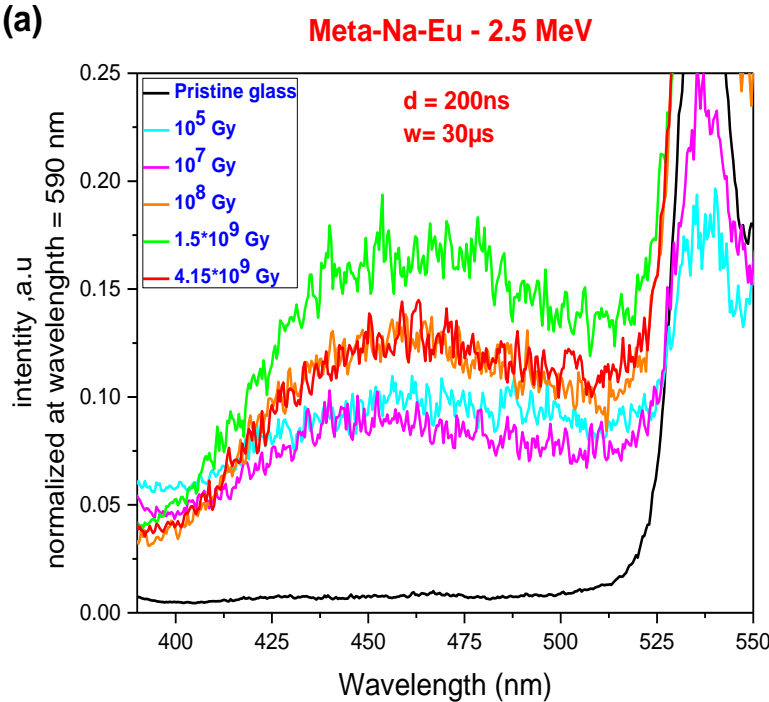


Figure 2

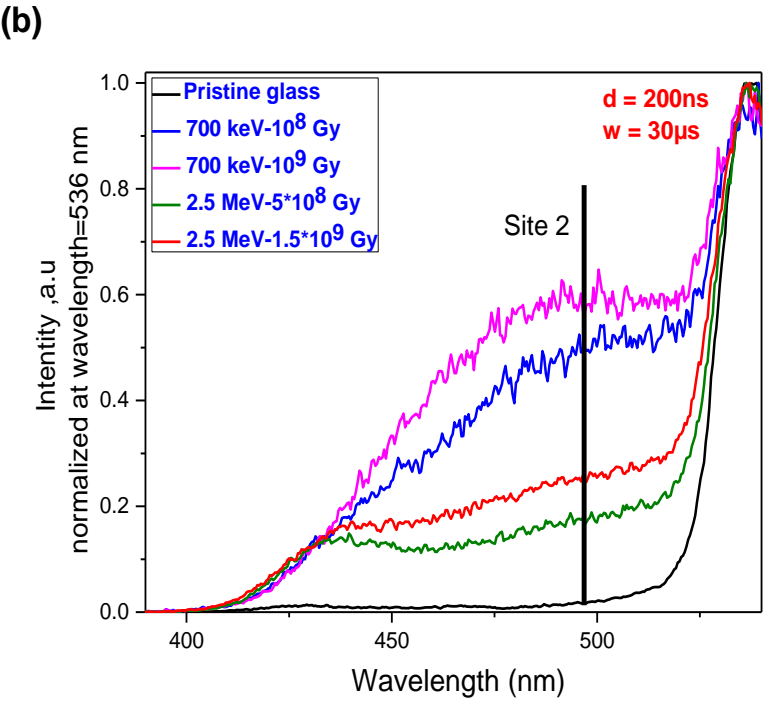
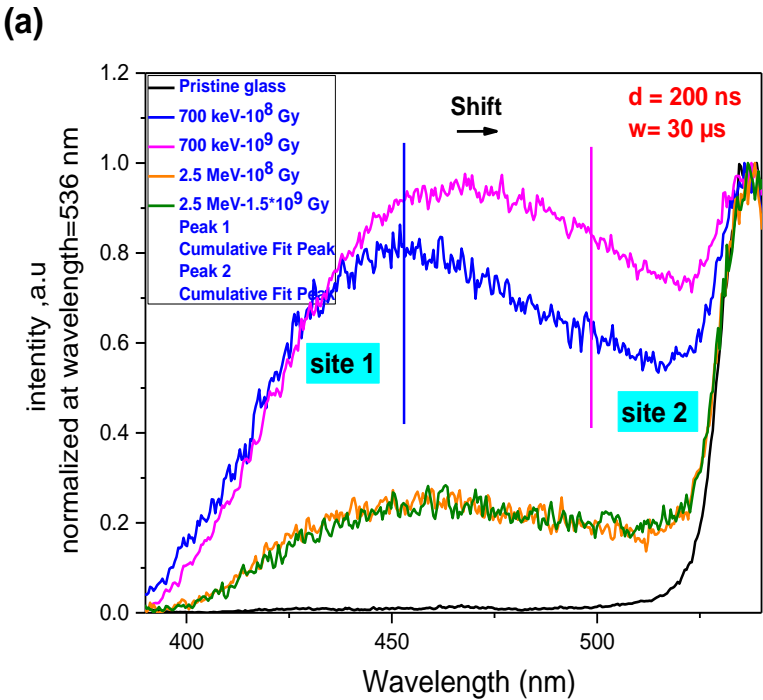


Figure 3

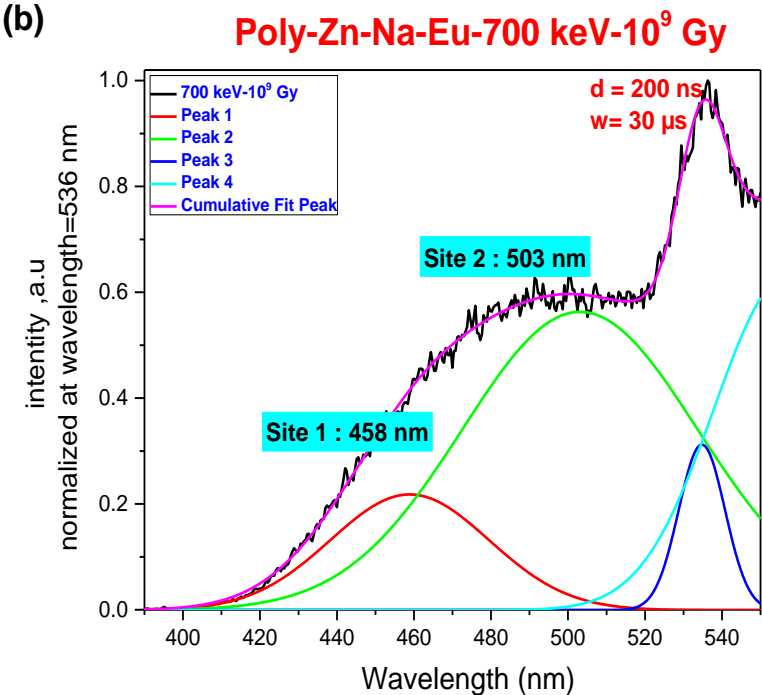
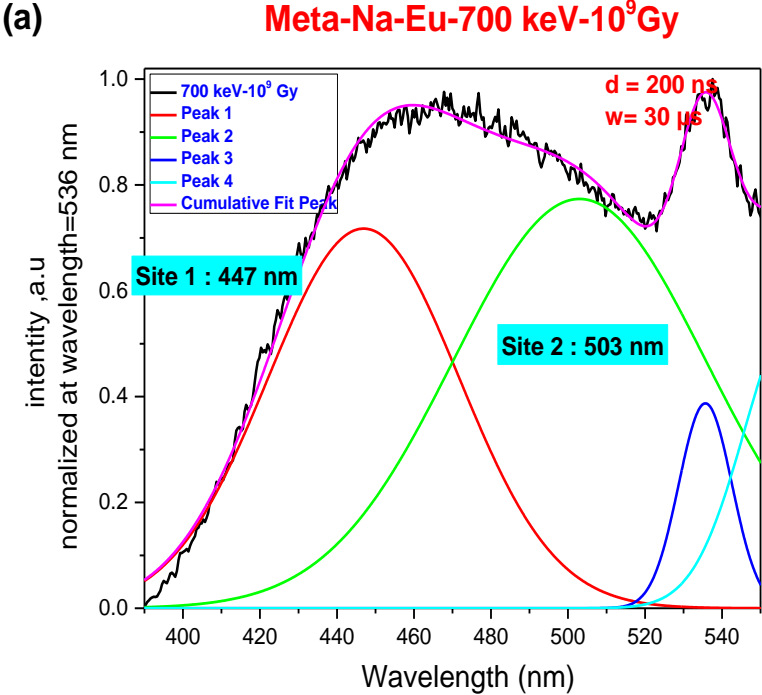


Figure 4

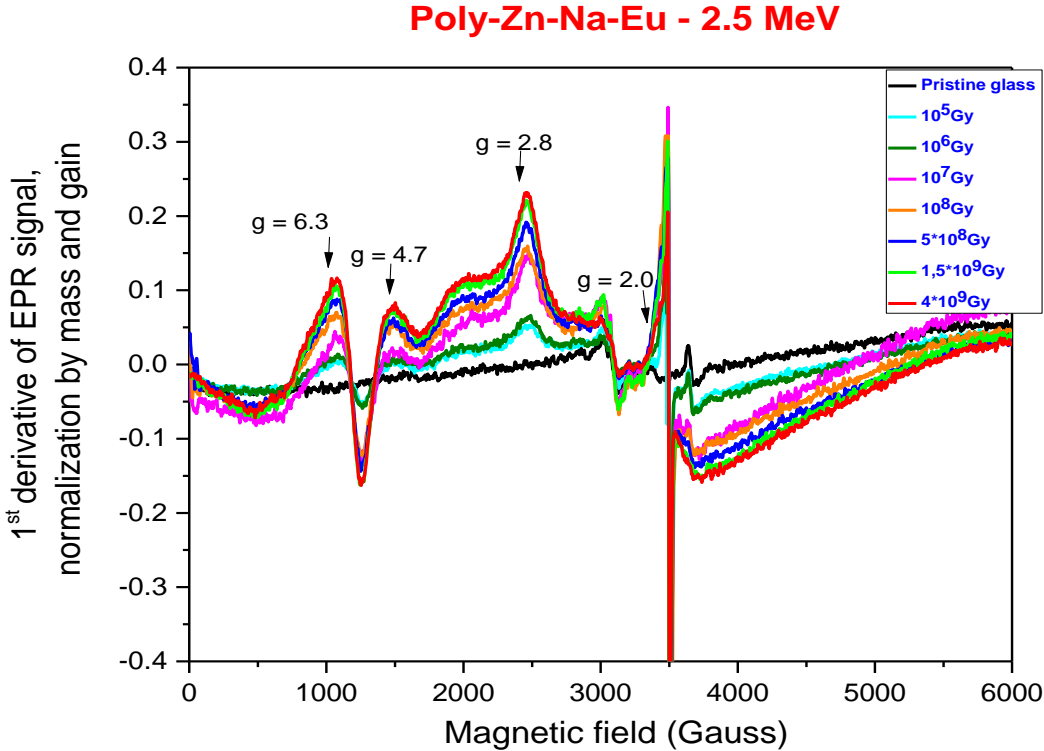


Figure 5

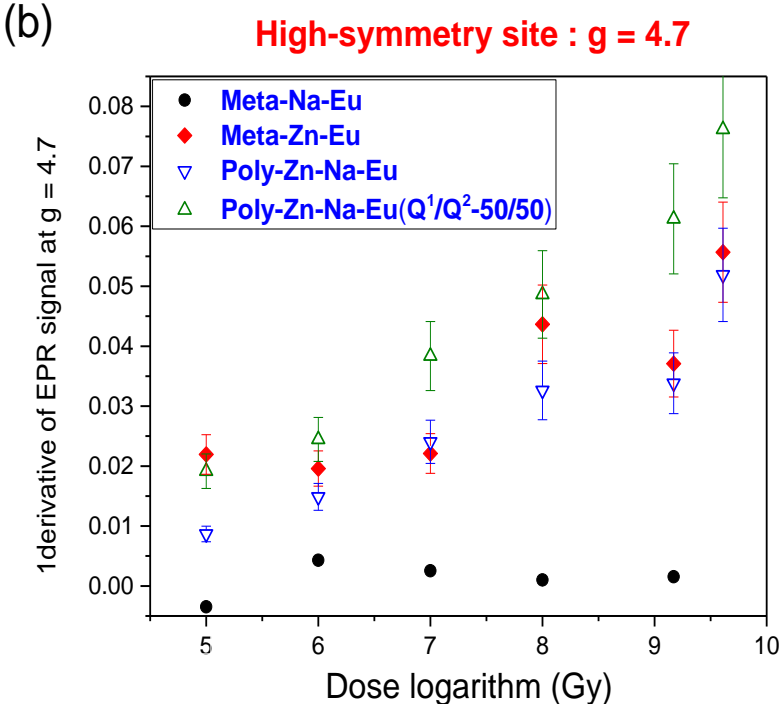
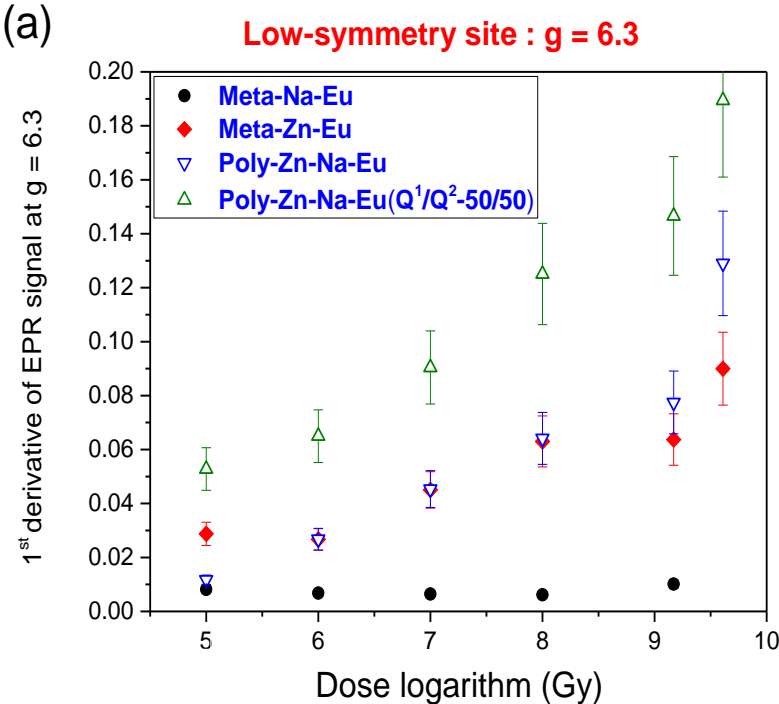


Figure 6

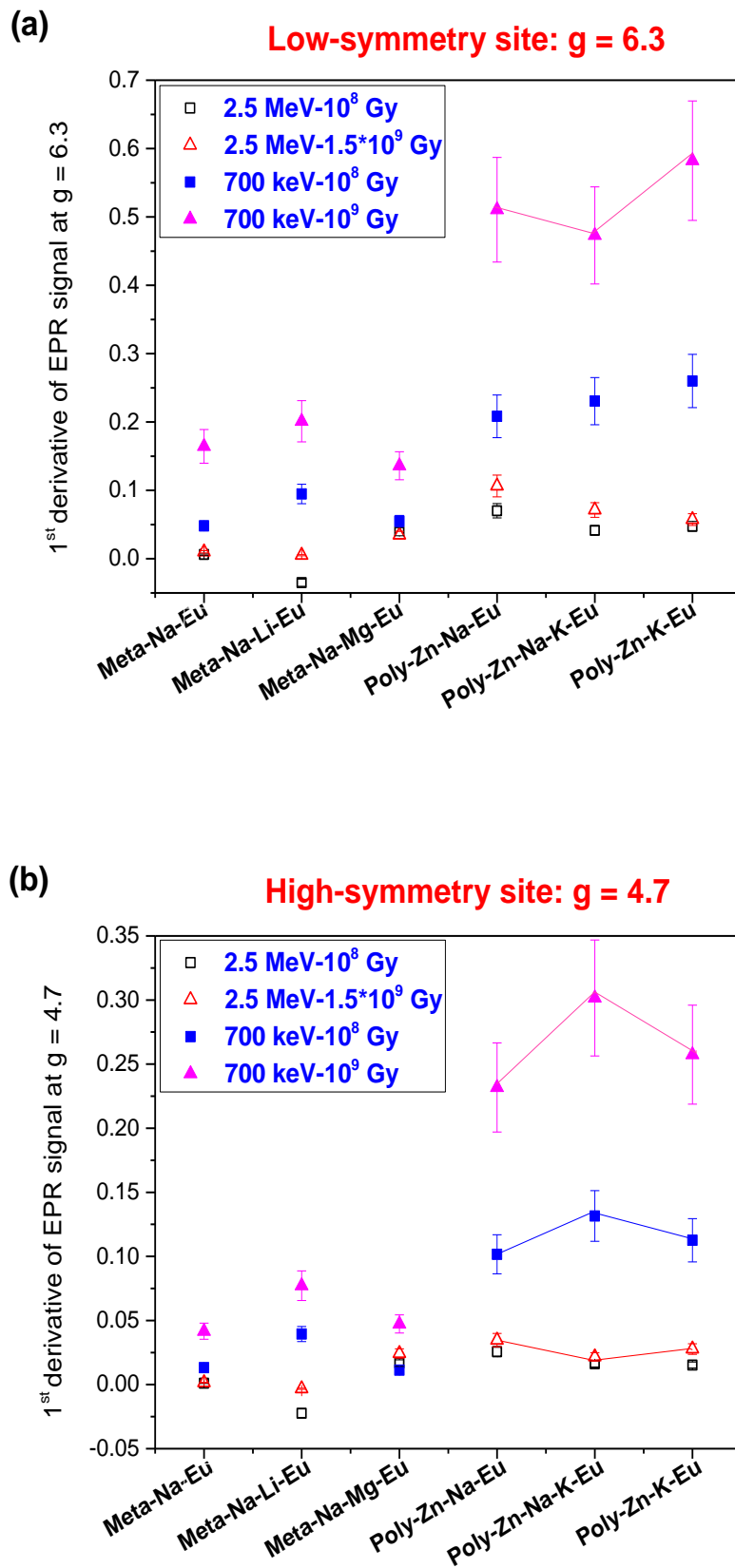


Figure 7

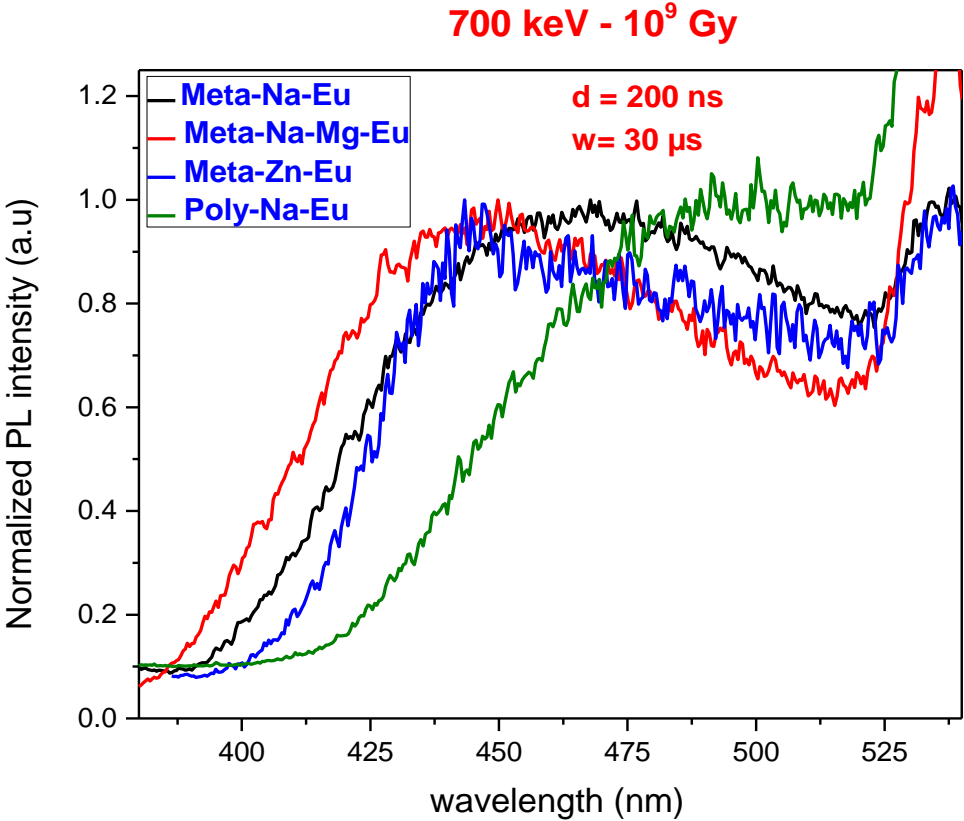


Figure 8

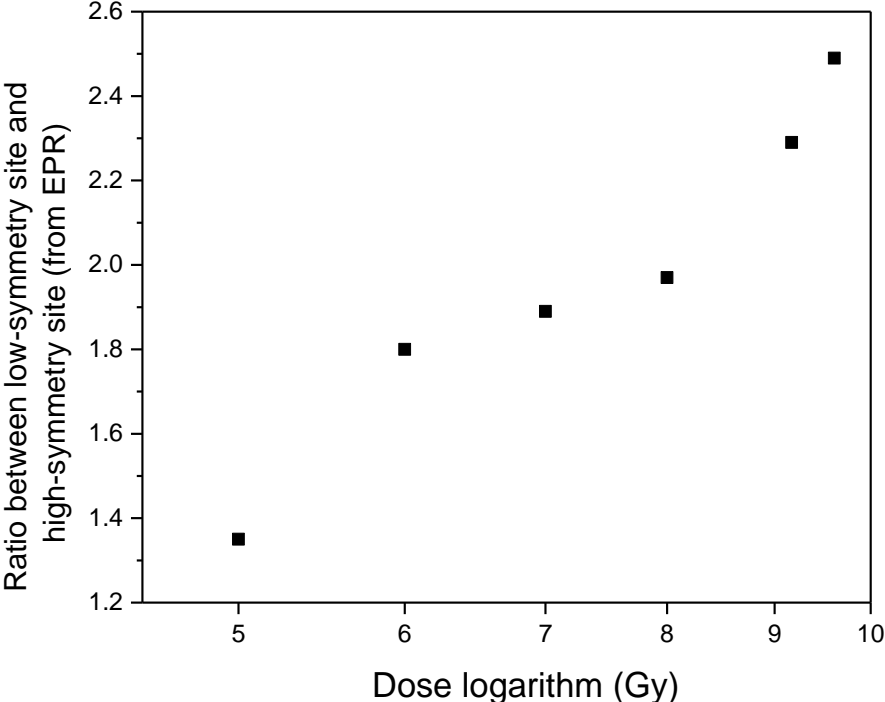


Table 1

Samples	Mol.%						
	P ₂ O ₅	Na ₂ O	Li ₂ O	K ₂ O	ZnO	MgO	Eu ₂ O ₃
Metaphosphate glasses							
Meta-Na-Eu	49.40	49.40					1.20
Meta-Na-Li-Eu	49.40	24.70	24.70				1.20
Meta-Na-Mg-Eu	49.40	32.90				16.50	1.20
Meta-Zn-Eu	49.40				49.40		1.20
Polyphosphate glasses							
Poly-Zn-Na-Eu	33.00	19.80			46.00		1.20
Poly-Zn-K-Eu	33.00			19.80	46.00		1.20
Poly-Zn-K-Na-Eu	33.00	9.90		9.90	46.00		1.20
Poly-Zn-Na-Eu(Q ¹ /Q ² :50/50)	39.52	38.52			19.76		1.20

Table 2

700 keV-10⁹Gy				
	Low-symmetry site	High-symmetry site	Symmetry Ratio	ZnO (mol. %)
Meta-Na-Eu	0.16 ± 0.02	0.04 ± 0.01	3.92	-
Meta-Na-Mg-Eu	0.14 ± 0.02	0.05 ± 0.01	2.88	-
Poly-Zn-Na-Eu	0.51 ± 0.08	0.23 ± 0.03	2.20	49.40
Meta-Zn-Eu	0.08 ± 0.01	0.08 ± 0.01	1.06	46.00