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# PHOTOLUMINESCENCE STUDY OF Eu-SPECIES INCORPORATED IN LITHIUM TETRABORATE AND SILICA

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*Steady-state – excitation and emission – photoluminescence spectra of europium species incorporated in single crystal and glassy lithium tetraborate (LTB) and silica are reported. Kinetic features, decay curves of the emission and lifetime data were measured. Spectral characteristics were analyzed with the aim of distinguishing the oxidation state, site-symmetry and morphology of europium species in different solid-state host matrices.*

## INTRODUCTION

During many years the development of advanced solid – state materials was very intensive as being highly requested. Wide application of such materials as luminescent lamp, X-ray intensifying screens for medical purposes, color television tubes, etc. is known.

Considerable progress in the field of luminescent materials was made by introduction rare earth (RE) ions as activators. Thus, red-emitting europium phosphor –  $Y_2O_3:Eu$  in color television tube was a real break through.

Unique photoluminescence features of europium ions can be used for reliable distinguishing of their valence state, site-symmetry and morphology of Eu-ions in the host lattice. Photoluminescence of  $Eu^{2+}$  and  $Eu^{3+}$  ions shows the apparently different spectral pattern – energy position and shapes – and kinetic characteristics, lifetimes.

Thus, blue single-band photoluminescence of  $Eu^{2+}$  ion arises from  $4f^7 \rightarrow 4f^6d^1$  interconfigurative transition and displays fluorescence lifetimes in microsecond range while  $Eu^{3+}$  ion exhibits the red sharp line fine-structured spectra with phosphorescence lifetimes in the range of milliseconds. There are numerous publications devoted to the problem reviewed in detail in the monograph [1]. The Table reflects the relevant data.

**Table.** Photoluminescence features of europium ions

Ion	Electron transitions	Wavelength ( $\lambda$ ) of emission	Type of emission and lifetime ( $\tau$ ) of excited state
$Eu^{2+}$	$4f^7 \rightarrow 4f^6d^1$	370–450 nm (monoband)	fluorescence, microseconds ( $\mu s$ )
$Eu^{3+}$	$^5D_0 \rightarrow ^7F_j$	580–750 nm (fine-structured line emission)	phosphorescence, milliseconds (ms)

In our previous study addressed to photoluminescence characterization of Eu-species incorporated into polycrystal of oxide ( $Y_2O_3:Eu$ ), phosphate ( $Sr_3(PO_4)_2:Eu$ ) and fluorochloride ( $BaFCl:Eu$ ) lattices it was revealed that the oxidation states ( $Eu^{2+}$  or  $Eu^{3+}$ ) and morphology (isolated ions or clusters) strongly determine photoluminescence spectral patterns, lifetimes data, and quantum efficiency [2].

An idea of this study is to use Eu-ion photoluminescence spectral features for discrimination of different states of Eu-ions incorporated in solid matrices. It will be considered such photoluminescence characteristics as

- spectral pattern;
- resolution;
- intensities distribution;
- lifetime data.

Thus, the task of the study is a comparative photoluminescence investigation of Eu-species in such materials:

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1. Eu-species in single crystals  $\text{Li}_2\text{B}_4\text{O}_7$  (LTB) and  $\text{Bi}_{12}\text{GeO}_{20}$  (BGO);
2. Eu-species in  $\text{Li}_2\text{B}_4\text{O}_7$  (LTB) glass;
3. Eu-nanoparticles in silica glass.

It is important to note that the presence of nanoparticles in silica glass was confirmed by TEM-technique.

### SAMPLES AND TECHNIQUES

Single crystals of LTB:Eu were grown by the Czochralski method from high purity precursor compounds. Glassy samples were prepared by melting part of doped single crystal to ensure the same dopant content. Concentrations of Eu in the samples estimated by neutron activation analysis were found to be 0.0016–0.008 wt% Eu [3].

Doped silica samples were produced by chemical vapor deposition technique, sol-gel procedure and thermal treatment [4].

Photoluminescence spectra were recorded with a Perkin-Elmer LS50B luminescence spectrometer equipped with a pulsed xenon lamp. Instrument can to perform phosphorescence measurements using selectable time delays between excitation and detection.

### RESULTS AND DISCUSSION

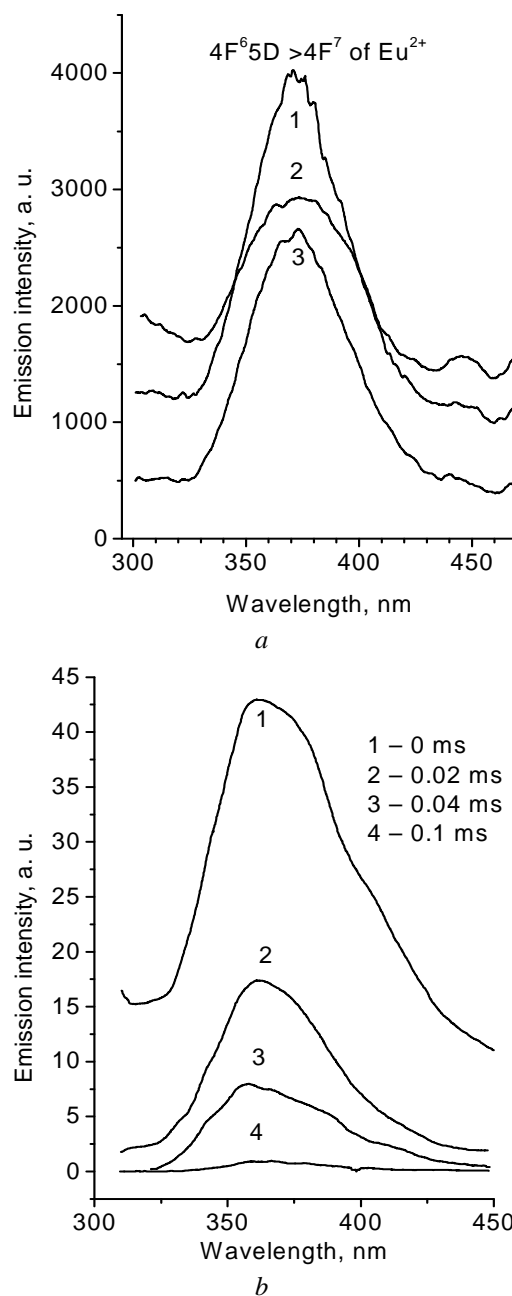
Fig 1a displays photoluminescence spectra of LTB:Eu single crystals. Important to note that the three spectra relate to the three separate growth of single crystals. It is seen that these spectra are essentially similar and consist of single band emission at about 370 nm arising from interconfigurative  $4f^7 \rightarrow 4f^65d^1$  transition.

Fig 1b presents emission spectra of LTB:Eu single crystal measured at various time delays between excitation and detection. Evident decrease in fluorescence is consistent with the evaluated lifetime value of this band that proved be 24  $\mu\text{s}$ .

Such spectral features: energy position, shape and lifetime strongly point that the isolated  $\text{Eu}^{2+}$  ions are the luminescence centers in LTB:Eu single crystal.

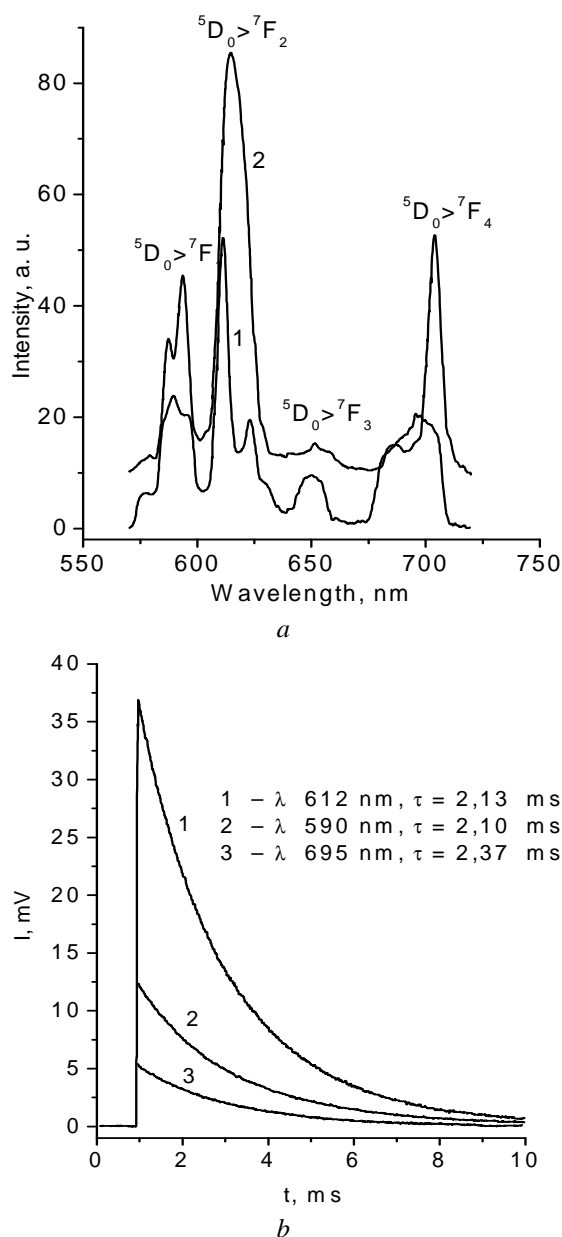
Very similar photoluminescence spectral features of Eu-doped luminophors are reported in literature. Thus Eu-doped novel scintillator  $\text{LiCaAlF}_6$  single crystal exhibited intense monoband luminescence at 370 attributed to  $\text{Eu}^{2+}$  ions [5].

Recently the presence of  $\text{Eu}^{2+}$  ions was obtained in the LTB:Eu glass samples grown in reducing conditions or after  $\gamma$ -irradiation [6].



**Fig. 1.** *a* – Emission spectra of  $\text{Li}_2\text{B}_4\text{O}_7$ :Eu single crystal of various growth and different Eu content: 1 – 0.008, 2 – 0.004, 3 – 0.0016 wt.%. Excitation at 250 nm; *b* – Emission spectra of  $\text{Li}_2\text{B}_4\text{O}_7$ :Eu single crystal measured at various time delays between excitation and detection

Single bands at 385 nm and 420 nm were revealed in the photoluminescence spectra of  $\text{BaFCl}:\text{Eu}$  and  $\text{Sr}_3(\text{PO}_4)_2:\text{Eu}$  polycrystal samples, respectively and attributed to isolated  $\text{Eu}^{2+}$  ions which substituted Ba or Sr ions in the lattices [2].



**Fig. 2.** *a* – Photoluminescence of  $\text{Eu}^{3+}$  species in crystals: 1 –  $\text{Bi}_{12}\text{GeO}_{20}$ , (single crystal, excitation at 330 nm); 2 –  $\text{Li}_2\text{B}_4\text{O}_7$  (polycrystal, excitation at 250 nm); *b* – Emission decay curves and lifetimes of  $\text{Li}_2\text{B}_4\text{O}_7:\text{Eu}$  glass sample at different wavelengths emission.

Photoluminescence emission spectrum of LTB:Eu glassy (as well as spectrum of LTB:Eu polycrystal sample) are completely different as compared to spectrum of single crystal (Fig. 2*a*, spectrum 2). Well-structured line emission of  $^5\text{D}_0 \rightarrow ^7\text{F}_j$  transitions in the range of 580–700 nm is observed. Such spectral pattern is typical of  $\text{Eu}^{3+}$  ions [1].

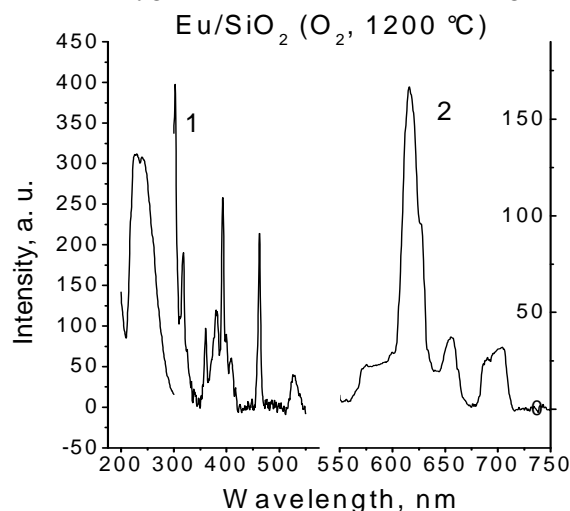
Intensities distribution within the spectrum gives information about the site-symmetry of emitting  $\text{Eu}^{3+}$  ions. High ratio of intensities – electric-dipole  $^5\text{D}_0 \rightarrow ^7\text{F}_2$  transition to magnetic-dipole  $^5\text{D}_0 \rightarrow ^7\text{F}_1$  gives evidence of low site-symmetry of  $\text{Eu}^{3+}$  ions in this lattice.

Photoluminescence spectrum of BGO:Eu single crystal (Fig. 2*a* spectrum 1) displays another features. Individual  $^5\text{D}_0 \rightarrow ^7\text{F}_j$  transitions are narrower and better resolved. In this case the intensities of  $^5\text{D}_0 \rightarrow ^7\text{F}_2$  and  $^5\text{D}_0 \rightarrow ^7\text{F}_1$  are comparable that implies higher (with inversion centre) site symmetry of  $\text{Eu}^{3+}$  ion that substitutes  $\text{Bi}^{3+}$  ion in the lattice [7].

Additional information about the state of  $\text{Eu}^{3+}$  ions in LTB host can be derived from emission decay curves measured at wavelength of main transitions:  $^5\text{D}_0 \rightarrow ^7\text{F}_1$  (590 nm),  $^5\text{D}_0 \rightarrow ^7\text{F}_2$  (612 nm) and  $^5\text{D}_0 \rightarrow ^7\text{F}_4$  (695 nm). Fig 2*b* presents these data. Obtained values of lifetime are in millisecond range that is in agreement with phosphorescence type of  $\text{Eu}^{3+}$  ions emission. The attention deserves that the lifetime values for these transitions appeared to be practically identical that strongly points to one (or very similar in coordination) type of  $\text{Eu}^{3+}$  emitting ions.

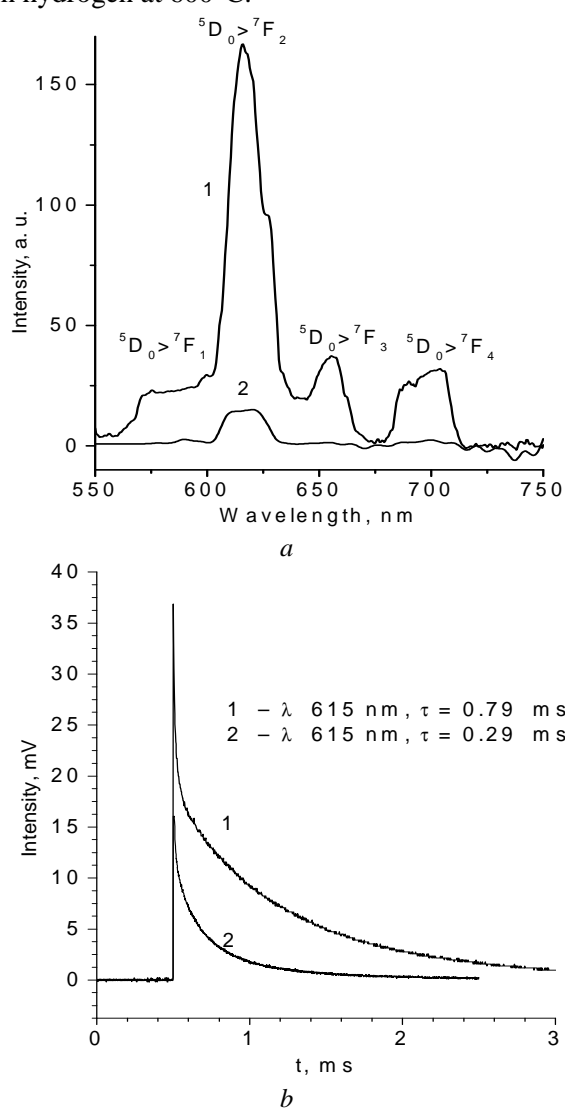
Thus we suggest that the isolated  $\text{Eu}^{3+}$  ions incorporated in the interstitial positions are responsible for observed photoluminescence characteristics of LTB:Eu polycrystal and glassy samples.

Photoluminescence – excitation and emission – spectra of Eu nanoparticles in silica glass treated in oxygen at 1200°C are shown in Fig. 3.



**Fig. 3.** Photoluminescence of  $\text{Eu}^{3+}$  nanoparticles in silica glass: 1 – excitation spectrum (monitoring emission at 615 nm), 2 – emission spectrum (excitation at 250 nm)

Excitation spectrum  $I$  consists of broad charge transfer ( $O^{2-} \rightarrow Eu^{3+}$ ) band peaked at 250 nm and sharp lines of f-f transitions. Emission spectrum dominates with  ${}^5D_0 \rightarrow {}^7F_2$  transition that is consistent with the low site-symmetry of  $Eu^{3+}$  in the nanoparticles. It is seen that the photoluminescence emission spectrum of Eu nanoparticles in silica displays the broadening of individual lines f-f transitions and decreasing of resolution as compared to  $Eu^{3+}$  monospecies. Fig. 4 presents the comparison of photoluminescence emission spectra of Eu nanoparticles in silica glass samples treated in oxygen at 1200°C and in hydrogen at 600°C.



**Fig. 4.** *a* – photoluminescence of  $Eu^{3+}$  nanoparticles in silica glass samples: 1 – treated at 1200°C under  $O_2$ , 2 – treated at 600°C under  $H_2$ ; *b* – emission decay curves of samples 1 and 2, respectively

Essential photoluminescence intensity decrease was observed in the sample treated in hydrogen at 600°C (Fig. 4, spectrum 2). This observation may be caused either with decreasing of emission  $Eu^{3+}$  ions in the result of recharging  $Eu^{3+} \rightarrow Eu^{2+}$  in reducing atmosphere or quenching emission of  $Eu^{3+}$  by OH groups. To make the choice between these possible reasons the additional study is requested.

Emission decay curves (at  $\lambda$  615 nm) of above samples are shown on Fig 4*b*. Remarkable lifetimes decrease to 0.79 and 0.29 ms in the  $Eu/SiO_2(O_2)$  and  $Eu/SiO_2(H_2)$  samples was revealed. This observation clearly points to either energy transfer between  $Eu^{3+}$  ions in nanoparticles or increasing of non-radiative relaxation.

## CONCLUSION

Analysis of obtained photoluminescence characteristics, namely spectral pattern, resolution, intensities distribution and lifetime data allows us to conclude that:

- in LTB single crystal Eu is incorporated as  $Eu^{2+}$  ions, showing single band emission at 370 nm with  $\tau$  24  $\mu s$ . In all other materials europium is present as  $Eu^{3+}$  species;
- in the both LTB (glassy, polycrystal) and BGO single crystal photoluminescence of  $Eu^{3+}$  displays fine-structured line emission in the range 580–700 nm.  $Eu^{3+}$  ion in BGO substitute  $Bi^{3+}$  ion and occupies site with inversion symmetry, while in LTB (glassy, polycrystal)  $Eu^{3+}$  ion is most probably situated in the interstitials with very low site symmetry. Lifetime data appeared to be in the range of 2.13–2.37 ms that are typical for isolated of  $Eu^{3+}$  ions.

Photoluminescence of Eu nanoparticles in silica displays broadening of individual lines of f-f transitions and decreasing of resolution as compared to isolated  $Eu^{3+}$  ions. Remarkable lifetimes decrease to 0.79 and 0.29 ms in the samples  $Eu/SiO_2(O_2)$  and  $Eu/SiO_2(H_2)$ , respectively was revealed that points either to energy transfer between  $Eu^{3+}$  ions or increasing of non-radiative relaxation processes in  $Eu^{3+}$  nanoparticles.

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**Фотолюмінесцентне дослідження європію, інкорпорованого в літій тетраборат та кремнезем**

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*Досліджено спектри стаціонарної фотолюмінесценції (збудження та випромінювання) європію, інкорпорованого в монокристалічний і полікристалічний літій тетраборат та кремнезем. Приведено дані кінетичної фотолюмінесценції: криві загасання та час життя збудженого стану іонів європію в зразках. Проведено аналіз спектральних характеристик з метою визначення стану інкорпорованих іонів європію – окислювального та агрегатного, а також локальної симетрії в різних матрицях.*

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*Исследованы спектры стационарной фотолюминесценции (возбуждения и излучения) европия, инкорпорированного в монокристаллы и поликристаллы литий тетрабората и кремнезема. Приведены данные кинетической фотолюминесценции: кривые затухания и время жизни возбужденного состояния ионов европия в образцах. Проведен анализ полученных спектральных характеристик с целью определения состояния инкорпорированных ионов европия – окислительного и агрегатного, а также локальной симметрии в разных матрицах.*