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Luminescent properties of lithium-phosphate-borate glasses doped with Tb^{3+}/ Eu^{3+} ions

D T Valiev[1], S A Stepanov and Liu Cong

Department of Lasers and Lighting Engineering, Institute of High Technology Physics, National Research Tomsk Polytechnic University, 30 Lenin Avenue, Tomsk 634050, Russia

E-mail: dtdamirka@gmail.com

Abstract. The luminescence of Li_2O-B_2O_3-P_2O_5-CaF_2 scintillation glass doped Tb^{3+}, Eu^{3+} under different types of excitation sources are investigated. Changing the europium concentration of 0.5 to 1 wt% leads changes in luminescence intensity of Tb^{3+} ions. The luminescence spectrum of the Tb^{3+} ions are depend on the concentration of Eu^{3+}. It was found, that the luminescence decay kinetics of terbium ion in the band 543 nm depending on the concentration of europium and from type of excitation. The difference in the nature of the luminescence decay kinetics of glasses under pulsed photo- and electronic excitation discussed.

1. Introduction

To date, the most promising pair of rare-earth ions (REI) that act as activators, ions is terbium (Tb^{3+}) and europium (Eu^{3+}), which are very intensively studied in a variety of amorphous systems of complex composition [1]. Interest in such systems is due to the widespread use of phosphors and scintillator materials, activated a couple of Tb-Eu, in scientific and technological fields [2]. For example, glass doped with terbium, are used in radiography as thermal neutron detectors due to their unique optical properties [3].

The trivalent ions of terbium (Tb^{3+}) cause luminescence in the visible range due to optical transitions $^5D_4 \rightarrow {}^7F_J$ (J = 2, 3, 4, 5, 6), the most intense of which is the transition $^5D_4 \rightarrow {}^7F_5$, corresponding to a wavelength of 544 nm radiation. Intense luminescence of terbium ions is observed in many hosts, for example, aluminum oxide films [4]. In order to improve the luminescent characteristics of terbium ions are added to the host material other ions, which, through various mechanisms can transfer excitation energy to luminescence centers. Among the REI doped, Eu^{3+}/Tb^{3+} co-doped compounds have received considerable interesting due to their following potential luminescent properties in phosphors: the Eu^{3+} ions emit red emission at 614 nm ($^5D_0 \rightarrow {}^7F_2$ transition) and Tb^{3+} ions emit green emission at 544 nm ($^5D_4 \rightarrow {}^7F_5$ transition), which make up the disadvantage of low color rendering index due to the lack of a green emission in most white LEDs fabrication process.

Most published studies are limited to the study of optical properties of materials containing different promoters. Remain insufficiently studied spectral and decay kinetic characteristics of scintillation glasses. A more detailed discussion of this issue will improve the understanding of the mechanisms of interaction between the ions of the activators and help with the decision of applied

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problems related to the study and development of new materials with predetermined properties, as well as to seek opportunities synthesis of radiation-sensitive material by introducing these adjuvants.

2. Experimental details

2.1. Glass preparation

In the present work glass system of the composition Li_2O-B_2O_3-P_2O_5-CaF_2 (LBPC) doped with Tb 5 wt%:X wt% Eu where X= 0.5, 0.7 and 1 (Table 1). The samples were synthesized at the Institute for Single Crystals of the National Academy of Sciences of Ukraine (Kharkov). For glass synthesis the following compounds were chosen: $LiPO_3$, H_3BO_3, CaF_2, Eu_2O_3 and Tb_2O_3. All the reagents were high purity used without further purification. The resulting glasses are found to be homogeneous, transparent and moisture resistant. The composition of the samples is given in Table 1.

Table 1. Composition of the tested scintillating glasses

Sample	Composition, weight %				
	Eu	Tb	CaF_2	H_3BO_3	$LiPO_3$
LBPC:Tb5Eu0.5	0.5	5	10	10	to 100
LBPC: Tb5Eu0.7	0.7	5	10	10	to 100
LBPC: Tb5Eu1	1	5	10	10	to 100

The major component of all the prepared glasses was lithium metaphosphate. It was chosen due to its low melting point and high solubility to different oxides and salts. This property facilitates the modification of glass composition and incorporation of a large amount of dopants. Lithium metaphosphate was made by melting lithium dihydrogen phosphate (LiH_2PO_4) powder at 900 °C in a platinum crucible for 40 minutes. The molten mass was poured into a glassy carbon crucible and cooled to room temperature. The obtained glass is then crushed and used a precursor for the batch preparation.

The melting temperature of REE oxides is in the range 1690-2400 °C. lithium metaphosphate well mixes with the REE oxides in the batch, wherein the melting point of the mixture reduces. Lithium has a high cross section of thermal neutrons capturing, lack of heavy element atoms in the host is also reason to choose lithium methaphosphate and the possibility of forming homogeneous optically transparent glass with the volume of a perfect working surface which need no mechanical treatment directly in crucibles.

The initial batch was melted and heat-treated in platinum and glassy carbon crucibles in a muffle furnace SNOL 7.2/1300. The temperature and melting time were optimized. Complete dissolution of the components occurs at temperatures above 900 °C. The melt is frequently stired at regular intervals to make it homogeneous. The initial temperature of the glassy carbon crucible in which glass casting was performed was varied to control the cooling rate of the melt. The technique for making glass castings was developed. The batch was first preheated at 800 °C in a muffle furnace. The temperature was raised up to 900 ... 1100 °C (depending on REE concentration). The melting time was 90 minutes. Melting at 900 °C allows addition of up to 2 wt. % of REE, and at 1100 °C up to 8–5 wt. % of REE can be added. The homogeneous melt was poured into the heated up to 200 °C glassy carbon crucible and cooled at room temperature. The prepared samples were colorless glass plates with a thickness of 3 mm.

2.2. Measurements

The integral luminescence spectra of pulsed cathodoluminescence (PCL) (“spectrum per pulse”) were recorded after electron beam excitation in the range of 300–900 nm with fiber optic spectrometer AvaSpec-2048. The integration time was from 1 ms to 10 ms. As a source of photoluminescence excitation ultraviolet LED light source (λ = 365 nm) and pulse nitrogen laser (λ = 337.1 nm) with 7 ns of pulse duration were used.

The PCL was studied by time-resolved spectrometry. For excitation was used electron source was a compact high-current accelerator of GIN-600 type with a vacuum diode. Duration of electron pulse at FWHM 10-15 ns, the average energy of the accelerated electrons was ~250 keV. The sample was placed in vacuum, the excitation energy density varied from 6 to 300 mJ/cm^2. The luminescence decay kinetics was recorded with a photomultiplier PMT-84-6 using monochromator MDR-3 and a digital oscilloscope LeCROY (350 MHz). Time-resolved measurement of the spectra was performed by scanning along the wavelengths and by recording the luminescence decay kinetics; the emission spectrum was reconstructed by the emission intensity at a given time I_t relative to the moment of the excitation pulse action (the time required to achieve the maximum amplitude of the electron beam current is assumed as t = 0).

3. Results and discussion

The optical transmission spectra of glasses are shown in figure 1. For all the investigated samples the transmission edge lies in the region of 350 nm. In the visible region the samples are transparent, i.e. the transmission coefficient is about 90%.

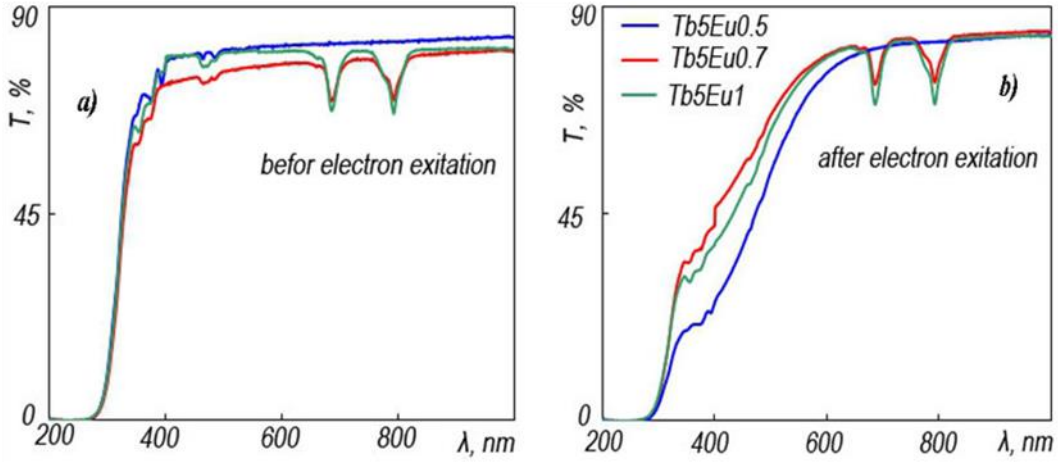

Figure 1. Optical transmission spectra LBPC: Tb, Eu glasses (a) with different concentration of Eu^{3+} ions; (b) glass irradiated with a pulse train (100 pulses) with the density of excitation energy of 69 mJ/cm^2

In the sample with the europium concentration of 0.7, 1 wt%, absorption peaks with maxima at 350, 367, 378 and 485 nm are recorded in the transmission spectrum which is apparently associated with f–f transitions in the terbium ion [5].

The transmission coefficient at 350 nm is 70%. The absorption peaks at 690 and 795 nm is recorded in samples which contain 0.7 and 1 weight% of europium ions (Figure 1). Increasing the concentration of europium ions results in the absorption of the bands (Figure 1a).

After irradiation with electron pulse train (100 pulses) it was observed a decrease of the samples transmittance. The absorption peaks in the range 350–378 nm could not be distinguished in the spectra of the irradiated samples (Figure 1, b). It was also found that the samples with the lowest concentration of europium are most sensitive to changes in the optical properties under electron irradiation.

When excited glass samples accelerated electron beam intense luminescence is observed whose spectrum consists of a series bands (Figure 2 a) with a peak wavelength of 489, 544, 588, and 620 nm, corresponding to radiative transitions in the ion Tb^{3+}:$^5D_4 \rightarrow {}^7F_6$, $^5D_4 \rightarrow {}^7F_5$, $^5D_4 \rightarrow {}^7F_4$, $^5D_4 \rightarrow {}^7F_3$.

For all samples the luminescence spectra is dominant in intensity in the “green” emission with λ_{max} = 544 nm. With increasing concentration of europium ions an increase in the intensity of luminescence of all major emission bands. Characteristic is the manifestation of luminescence band at

700 nm in a sample with a minimum concentration of europium Tb5Eu0.5. This band is due to the radiative transitions in europium ion $^5D_0 \rightarrow {}^7F_4$. The increase of Eu^{3+} leads to quenching of luminescence of europium in the band 700 nm.

When excited by a nitrogen laser glasses doped with europium and terbium ions was observed that an intense luminescence whose spectrum consists of a series bands corresponding to radiative transitions in the ion Tb^{3+} (Figure 2 b). The photoluminescence spectrum qualitatively similar to that of pulsed cathodoluminescence spectrum (PCL). However, in the spectrum of the radiation transition in europium ion $^5D_0 \rightarrow {}^7F_4$ at 700 nm is observed. Apparently this is due to the selectivity of the laser radiation. When excited glasses doped with europium heterostructure with λ = 365 nm (figure 2 c), the spectrum can be noted band 453 nm ($^5D_3 \rightarrow {}^7F_3$), which does not appear in the spectra of the PCL and under the excitation of nitrogen laser.

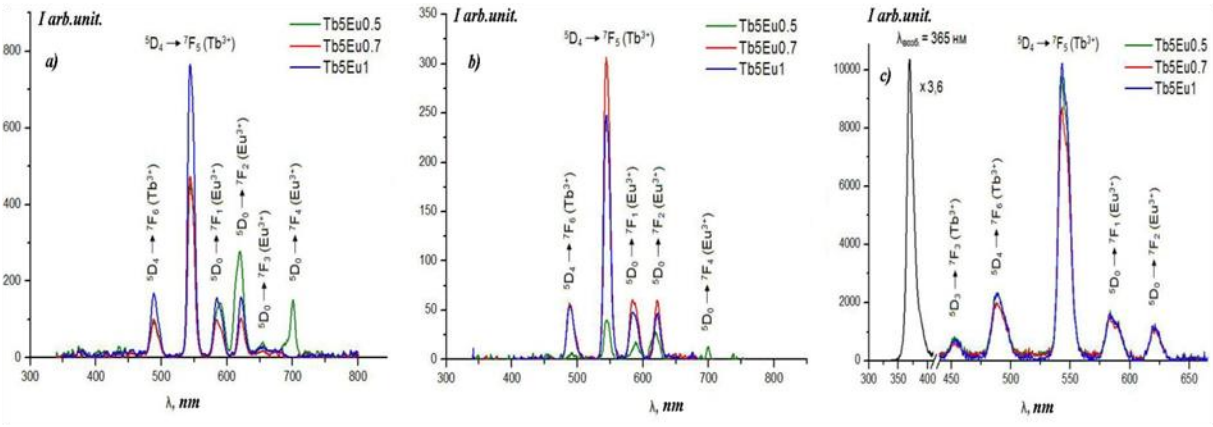

Figure 2. Luminescence spectra of LBPC:Tb5EuX (X=0.5; 0.7; 1) glasses measured by "spectrum per pulse" technique use different source of excitation: electron beam (a), nitrogen laser (λ = 337.1 nm) (b), LED chip (λ = 365 nm) (c)

Figure 3 shows the luminescence decay kinetics in the bands of 544 nm, the nature of which is related to the radiative transitions in terbium ions after exposed high-energy flow with nanosecond duration [6]. From the data obtained it can be noted that there are two components in decay kinetics: fast with the decay time $\tau_1 \sim 0.4$ ms and the slow component $\tau_2 \sim 1.8$ ms. Time characteristics are similar for all test glasses doped with REI in this type of excitation.

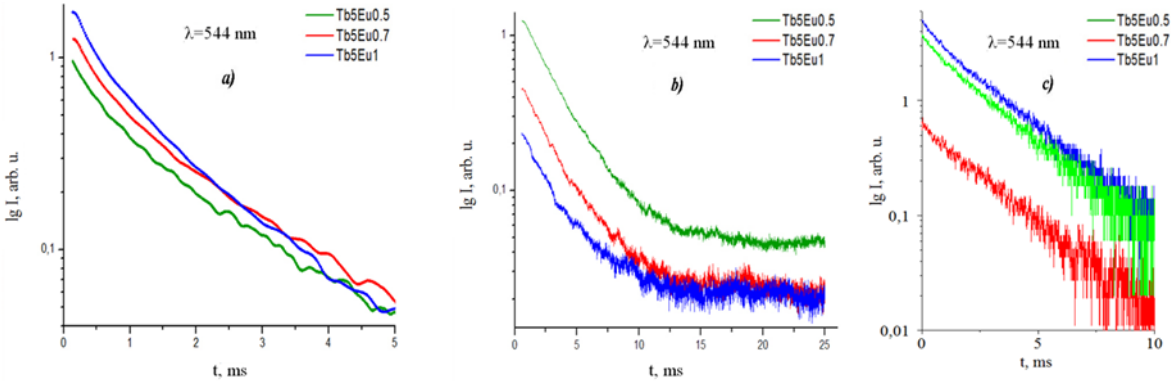

Figure 3. The luminescence decay kinetics curve of the of LBPC:Tb^{3+}, Eu^{3+} glasses (λ=544 nm) under electron (a), nitrogen laser (λ = 337.1 nm) (b) and LED chip (λ = 365 nm) excitation

Under photoexcitation (nitrogen laser pulses) the characteristic decay time of the long time component is comparable to the decay time of luminescence excited heterostructure (LED chip λ_{ex}=450 nm) τ is ~ 2.6 ms (table 2).

Table 2. Decay time of luminescence tested samples under different type of excitation

Type of excitation	Tb5Eu0.5		Tb5Eu0.7		Tb5Eu1	
	τ_1, ms	τ_2, ms	τ_1, ms	τ_2, ms	τ_1, ms	τ_2, ms
e-beam excitation	0,4	1,8	0,4	1,8	0,3	1,5
nitrogen laser (λ_{ex}=337 nm)	-	2,6		2.5		2.5
LED chip (λ_{ex}=450 nm)	0,8	2,7	1,2	2,9	0,6	2,6

The reason for the difference luminescence decay kinetics under pulsed photo- and electron excitation may be due to non-radiative transfer of excitation. When selective UV laser irradiation host glass excited weaker than in the case of high-current electron beam irradiation. As a result of the excitation of the host, are short-lived electronic excitations thus possible to increase the efficiency of nonradiative energy transfer to the host.

4. Conclusion

The performed studies demonstrate that lithium-phosphate-borate glass doped with Tb^{3+} and Eu^{3+} ions with different concentration has sufficiently effective luminescence upon excitation with a strong current electron beam, pulses of nitrogen laser and LED chip. The increase of europium content from 0.5 to 1wt% is cause the quenching of the emission bands at 700 nm of ions Eu^{3+}. On the other hand it leads to an increase in the intensity of luminescence bands in all major terbium ions. The bands of emission Tb^{3+} are dominating in luminescence spectrum. The luminescence decay time of terbium ions longer under photoexcitation, it is possible due to non-radiative energy transfer between ions co-activator. It was found, that the luminescence decay kinetics of terbium ion in the band 544 nm depending on the concentration of europium.

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