LUMINESCENT CHARACTERIZATION OF Eu-DOPED LATTICES

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Abstract

In the present paper a comparative spectral study – steady state and time-resolved photoluminescence (PhL) and radioluminescence (RL) – of Eu-doped phosphors in different host lattices: BaFCl, $Sr_3(PO_4)_2$, Y_2O_2S, Y_2O_3 is reported. Steady state and time-resolved (induced by X-ray tube, N_2-laser and high-energy accelerated electrons respectively) PhL and RL measurements were performed. Bright monoband and fine-structure line emissions in the blue-green and orange-red region were recorded in PhL and RL for all phosphors.

The spectroscopic investigation permits ode to deduce the following conclusions:

(i) The spectral patterns, decay curves and life-times observed in both PhL and RL are basically the same for all phosphors. On these observations it was assumed that similar luminescent species are involved in the both PhL and RL processes namely: mono-species Eu^{2+} and Eu^{3+} and their clusters.

(ii) Strong host-lattice influence on the status of Eu in the samples under consideration reflected in the spectral pattern, life-time and quantum efficiency was revealed.

Introduction

Europium-doped phosphors are subjects of very intensive spectroscopic studies. The reasons which stimulate enormous scientific interest can be explained by their unique characteristics. Firstly, these materials proved to be ideal for basic solid-state luminescence research such as : i) nature of electronic transitions and luminescence centres ii)mechanism and kinetics of excitation, energy transfer and emission processes [1]. The second reason is their extremely important practical applications in fluorescent lighting and in environmental, personal, clinical dosimetry [2-4].

Among the published numerous literature on luminescence spectroscopy of Eu-doped materials is distinguished the contribution of G. Blasse research group [1,5]. However, one can conclude that just the "classical" questions of Eu luminescence - the nature of emission centre, time-characteristics and quantum efficiency - are still the most topical and discussed [5]. Recent detailed studies evidenced about the complex structure of Eu luminescence centres which include Eu-dimers, clusters and Eu-O associates [6]. By time-resolved and site-selective spectroscopy several types of Eu centres have been discriminated [7].

The goal of this paper is the comparative PhL and RL investigation of Eu incorporated in different host-lattices. The study is aimed at revealing the site-structure (oxidation state; symmetry) and kinetic characteristics of Eu-species, involved in PhL and RL processes.

Experimental

Materials — four samples of Eu-containing phosphors such as BaFCl:Eu, $Sr_3(PO_4)_2$:Eu, Y_2O_2S:Eu, Y_2O_3:Eu have been studied. Europium-doped polycrystalline powders were laboratory obtained by the conventional solid state reaction; concentration of Eu near 0.5 mol % in all samples.

For the investigation the following techniques were used:

1. *Time-resolved photoluminescence (PhL) spectroscopy.* Kinetic measurements were performed on a spectroscopic set-up with an excitation pulse of N_2 laser (337 nm); half-width of pulse was equal 8 ns; time resolution 2 ns.
2. *Steady-state radioluminescence (RL)* spectra were measured using excitation of X-ray tube at 20 kV.
3. *Time-resolved radioluminescence (RL).* Excitation was induced by high-energy (4 Mev) electron pulses of linear electron accelerator (LINAC) with ~ 2.6 ms duration and ~100 Gy dose, time resolution 1ms.

Both PhL and RL measurements were performed at room temperature.

Results and discussion

Fig. 1a shows PhL spectrum for BaFCl:Eu sample. Fig. 2a displays the same data for Y_2O_2S:Eu phosphor. In Fig 1b and 2b are represented the decay curves of these two phosphors respectively. Fig. 3 contains RL spectra for all phosphors investigated. Fig. 4a-c represents the RL decay curves obtained under high-energy (4 MeV) electron excitation.

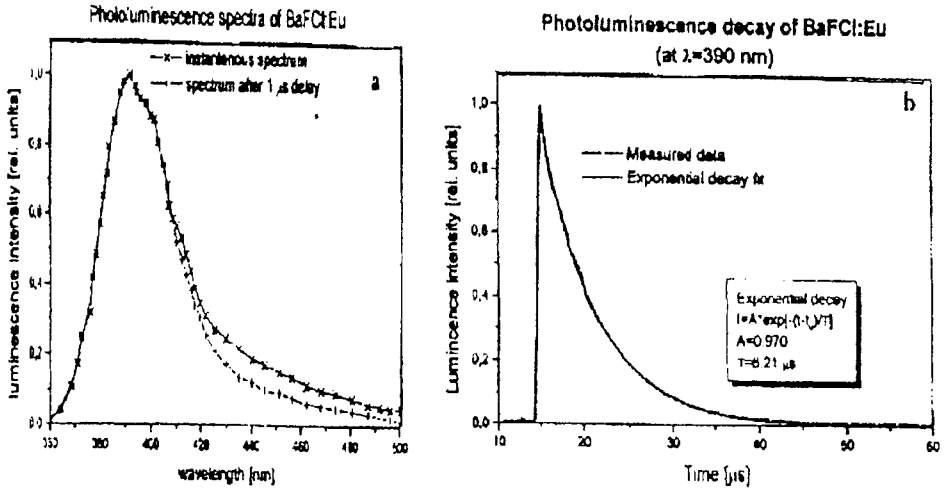

Fig. 1. Photoluminescence spectra of BaFCl:Eu (*a*) and decay at λ=390 nm (*b*)

As it is seen from the presented experimental data the studied phosphors show:

a) monoband emission PhL and RL (BaFCl:Eu, $Sr_3(PO_4)_2$:Eu, and Y_2O_2S:Eu);
b) fine-structure line emission in PhL and RL in the case of Y_2O_3:Eu.

It is important to notice that the spectral shapes registered in PhL and RL are practically the same for all investigated samples of *a)* group. It was also observed that for these

three phosphors the kinetic features - monoexponential decays and life-time values - are similar for the same sample in time-resolved PhL and RL.

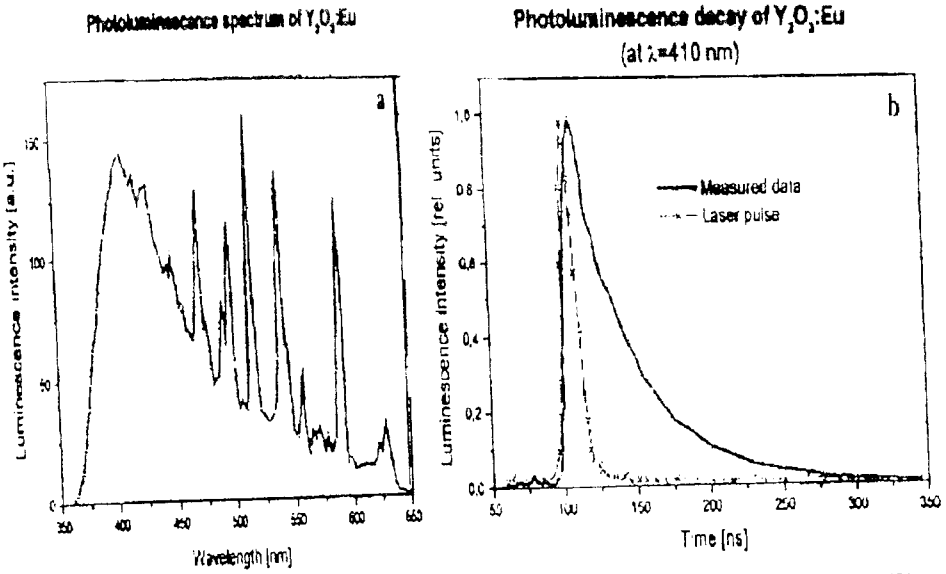

Fig. 2. Photoluminescence spectrum of Y_2O_3:Eu (*a*) and decay at λ = 410 nm (*b*)

However the presented spectral characteristics of the studied phosphors reveal also a certain differences. Different are the spectral patterns of time-resolved PhL and steady state RL for Y_2O_3:Eu that will be discussed further. Besides, as it is evident from Fig. 3 RL intensities are considerably different for investigated Eu-doped phosphors. As it can be seen from the summarizing Table the life times of the emitting Eu species are also essentially different — ranging from nanoseconds to milliseconds.

For discussing the nature of luminescent Eu species responsible for PhL and RL of the investigated phosphors all these experimental data must be taken into consideration. First of all, attention should be paid to the fact that the observed spectral patterns and kinetic data of emitting species for photoluminescence and radioluminescence for the same sample are basically the same for most of investigated phosphors except Y_2O_3:Eu. Thus the numerous literature on optical spectroscopy of europium species can be used for assignment of luminescent centres [1,5].

At the consideration of the oxidation state of Eu-species and the nature of the transitions connected with the observed spectra we have detected the following. Monoband blue emission peaking at 385-390 nm in PhL and RL spectra of BaFCl:Eu can be attributed to $4F^6 5D > 4F^7$ transition of mono-species of Eu^{2+} [8]. Position of luminescence bands, their mono-exponential decay and value for this sample nicely coincide in PhL and RL spectra and also with the data published for the single crystal phosphor of the same chemical composition [9]. Emission spectrum of $Sr_3(PO_4)_2$:Eu displays the red shift of the luminescence band and the considerably faster emission decay as compared to BaFCl:Eu.

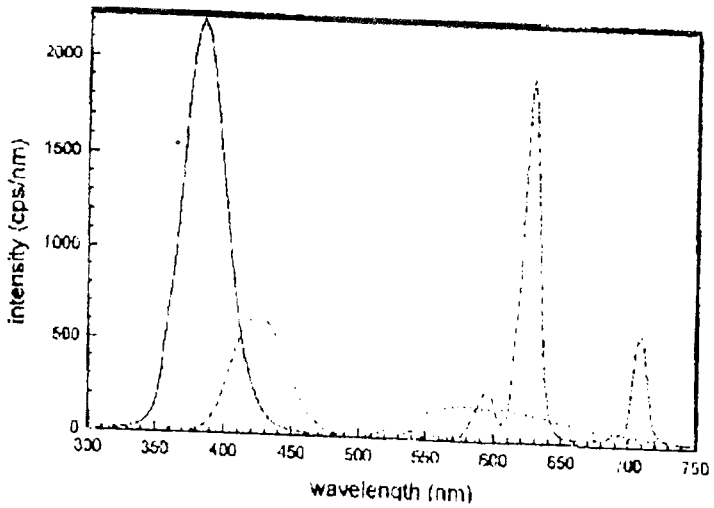

Fig. 3. Radioluminescence spectra of Eu-doped phosphors generated by X-ray excitation: solid line - BaFCl:Eu; dashed line - $Sr_3(PO_4)_2$:Eu; dotted line - Y_2O_3S:Eu; dash-dotted line - Y_2O_3:Eu.

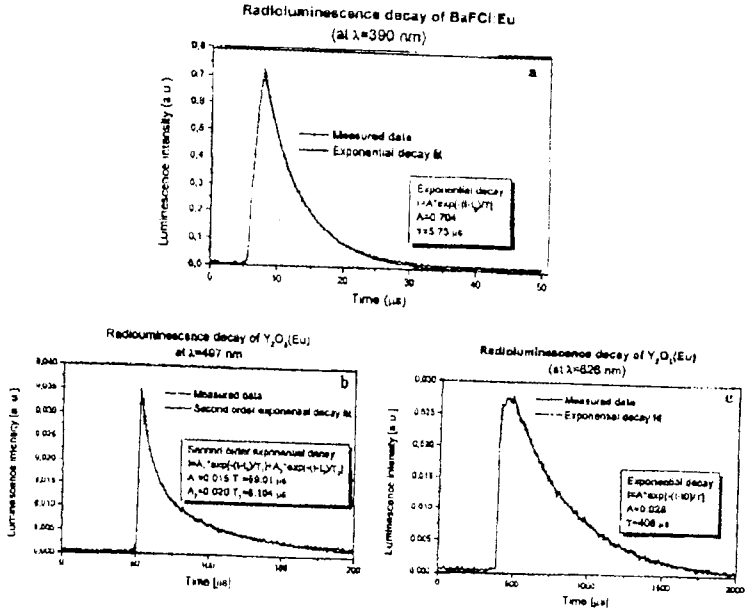

Fig 4. Radioluminescence decay curves of BaFCl:Eu at 390 nm (*a*); Y_2O_3:Eu at 497 nm (*b*) and at 626 nm (*c*).

It was reported that the clustering of Eu^{2+} in several host lattices was followed with the considerable red shift of emission band [10,11], thus it is very reasonable that changes in the Eu^{2+}-species aggregation status is responsible for these observations. Emission of Y_2O_3:Eu phosphor displays the most complicated spectral pattern: in time-resolved PhL it consists of monoband peaked at 410 nm and line fine structured spectrum in the 460-710 nm region (Fig. 2a). It should be noticed that the blue band at 410 nm disappears in PhL spectrum after 1 microsecond delay. Kinetic measurements (see curve 2b) revealed the fast decay of this emission - evaluated life-time is equal 41 ns. This short-living Eu species were not observed in the steady state of RL spectrum (see Fig. 3). Also it was not detected in the time-resolved RL as the time resolution of set-up used is in microseconds range.

The differences of line spectra in the PhL and steady state RL of Y_2O_3:Eu deserves further attention. Red RL is registered mainly in the 580-710 nm (see fig.3) while in the PhL spectrum fine-structured line emission is observed also in the 460-560 nm (see Fig 2a). The spectral pattern displayed in RL of Y_2O_3:Eu closely resembles the well-known characteristic line emitting transitions $^5D_0 \rightarrow {}^7F_0$, $^5D_0 \rightarrow {}^7F_1$, $^5D_0 \rightarrow {}^7F_2$ of Eu^{3+} centres. In this case the most intensive line in the RL spectrum is detected at 620 nm that corresponds to the $^5D_0 \rightarrow {}^7F_2$ electric dipole transition of Y_2O_3:Eu species with the low site symmetry.

Table
Spectral characteristics of Eu-doped phosphors

SAMPLE	PHOTOLUMINESCENCE		RADIOLUMINESCENCE		LUMINESCENT SPECIES
	max (nm)	life-time	Max (nm)	life-time	
BaFCl:Eu	385	6.3 μs	390	5,7 μs	Eu^{2+} monospecies
$Sr_3(PO_4)_2$:Eu	420	32 ns	425	- **	Eu^{2+} monospecies + Eu^{2+} pairs
Y_2O_2S:Eu	585*	67 ns	600*	- **	Eu^{2+} or/and Eu^{3+} clusters
Y_2O_3:Eu	410	t_1=41 ns			Eu^{2+}
	510		510	t_1=8.9 μs	***
	580		580		Superposition of Eu^{3+}
	620	t_2=10.2 μs	626	t_2=66.9 μs	monospecies of differe
	700	t_3=4000 μs	710	t_3=410 μs	site symmetry

* very broad unresolved band in the 500 -750 nm region
** cannot be measured with the facilities used
*** fine structure line emission in the region 460-560 nm tentatively is attributed to transitions from the higher excited levels $^5D_{1-3}$.

Less common observation in PhL spectral pattern was, in particular, line emissions blue-shifted from 580 nm ($^5D_0$ level). Tentatively we attribute these transitions from the higher exited levels: $^5D_{1-3}$ to $^7F_{0-4}$. Previously such transitions were registered in PhL spectra of Eu^{3+} doped rare-earth oxychlorides in [9] and quite recently in other Eu^{3+}-activated materials [12-15]. So it appears that for Y_2O_3:Eu phosphor the pattern in steady-state RL is caused by the most-

intensive transitions from $^5D_0$ level of only one type of Eu^{3+}species while the spectrum of time-resolved PhL includes also transitions from the higher excited levels - $^5D_{1-3}$ of several types of Eu^{3+}species.

Analyzing the spectral pattern of Eu^{3+} especially in PhL it seems that in our case it is caused by the superposition of several Eu^{3+} species of different site symmetry. Additional proof of this supposition can be obtained in complicated luminescence decay for different wavelengths that reveals the presence of emitting species with considerably different life-times (see Table).

These data allow to conclude the following:

i. For the same phosphor the spectral patterns, decay curves and life-times observed in the both PhL and RL are basically the same for all investigated phosphors. On these observations it was assumed that similar luminescent species are involved in the both PhL and RL processes namely: mono-species Eu^{2+} and Eu^{3+} and their clusters.

ii. The state of europium, doped in the different host-lattices, which is resembled in their spectral and kinetic characteristics, is substantially different.

It is important to notice that the different state of Eu species influenced by the host lattice causes the different emitting efficiency in RL of the phosphors investigated (Fig. 3).

Acknowledgements

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