

Enhanced light-emitting performances of Y₂O₃:Eu phosphor for FPD application.

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Abstract

Samples of yttrium oxide doped with trivalent europium have been prepared by ceramic techniques, under different synthesis conditions; barium chloride (BaCl₂) and sodium tetraborate (Na₂B₄O₇) were tested as flux. The improvement of luminescence properties in dependence on substitution of Eu³⁺ for Y³⁺ in the host lattice, under electron and UV excitations is demonstrated. The obtained results are discussed with respect to the employed processing method.

1. Introduction

There is a long interest in red emitting europium-activated yttrium oxide (Y₂O₃:Eu) both as a commercial phosphor, and as a model system for the study of the effect of the interplay of radiative and nonradiative processes on phosphor efficiency. The main applications of Y₂O₃:Eu as commercial phosphor are in lighting and cathode ray tube [1-3], display material [4-8], in tricolor fluorescent lamps [9], field emission displays [10], and laser devices.

The aim of this work is to synthesize europium-activated yttrium oxide phosphor with improved luminescence properties and to investigate these properties in dependence with their synthesis conditions. In order to enhance the luminescence of Y₂O₃:Eu and to improve the CIE coordinates, the thermal treatment in the presence of barium chloride (BaCl₂) and sodium tetraborate (Na₂B₄O₇) as flux is suggested. One attempt is also made to explain the photoluminescence (PL) and cathodoluminescence (CL) experimental data by proposing a relaxation model.

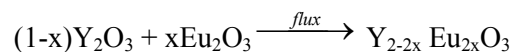
2. Experimental details

Phosphor samples were characterized by crystalline structure and luminescence properties.

Optical spectroscopy and PL characteristics were estimated on the basis of emission and excitation spectra registered at room temperature (Xe 500 W lamp) with DARSA PRO 5100 PL System (Professional Scientific Instrument Co, Korea). The excitation was performed with 254 nm and 365 nm UV radiation. Low temperature PL measurements (15 K) were carried out by using He-Cd laser as light source with 325 nm excitation wavelength. Low voltage (0.5-1 keV) CL was performed with the beam current density of 100 μA/cm² by using a Kimball Physics FRA2X1-2/EGPS-2X1 electron gun system.

3. Results and discussion

Different synthesis conditions were used to improve the light-emitting performances of Y₂O₃:Eu phosphor. Here we report on the influence of synthesis parameters on luminescence properties of Y₂O₃:Eu, prepared by solid state reaction. The phosphor formation during the firing stage could be described by the equation:



Barium chloride and sodium tetraborate (borax) were used as flux at temperature range 1100-1400°C. More than 20 Y₂O₃:Eu samples were prepared and investigated. XRD spectra of samples illustrate that all samples possess the cubic crystalline structure. The PL relative intensities of some phosphor samples prepared in various conditions are presented in table 1.

PL and CL measurements put in evidence the influence of thermal synthesis conditions on luminescence properties. The summarized data reveal the luminescence dependence on the annealing temperature, activator concentration and flux. The substitution of Eu^{3+} for Y^{3+} results in an increase in the doped phase unit cell volume as the concentration in Eu^{3+} increases. Difference in the ionic radii of yttrium and europium (1.02 Å and 1.07 Å, respectively in eightfold coordination) may account for this increase. Thus, the concentration dependence can be explained.

It has been obtained from all our measurements that the samples prepared with sodium tetraborate are more efficient than the corresponding material synthesized with barium chloride as flux and significantly better than the samples prepared without any flux.

The influence of annealing temperature on luminescence properties could be well observed (table 1) for 10% europium and BaCl_2 as flux. For the L10-L7-L12 series, the relative intensity increases with the annealing temperature.

To better understand the role of mineralizing agents and to explain the energy transfer in Eu^{3+} , the PL and CL spectra were registered. Emission and excitation PL spectra and some characteristic details at low temperature are presented in Figs. 1-4. Advantageous luminescence properties can be noticed for samples prepared with sodium tetraborate flux (L20 and L18, Fig.1).

All transitions from $^5\text{D}_0$ level occur between 570 and 720 nm and all lie in the visible region of the electromagnetic spectrum, resulting in red luminescence. The observed five broad bands located between 575-580, 580-603, 603-635, 640-665 and 680-715 nm, consisting from five groups of narrow lines each, could be easily assigned to $^5\text{D}_0 \rightarrow ^7\text{F}_{0-4}$ transitions of the Eu^{3+} ion. The weak emission in the vicinity of 580–600 nm is associated with the magnetic dipole transition $^5\text{D}_0 - ^7\text{F}_1$ (Fig.2). The strong emission around 610–630 nm is due to the hypersensitive electric dipole transition of $^5\text{D}_0 - ^7\text{F}_2$, induced by the lack of inversion symmetry at the Eu^{3+} site (Fig.3). Magnetic dipole transition and electric dipole transition are more efficient for L20 sample prepared with sodium tetraborate in comparison with L19, synthesized with barium chloride as flux. On the other hand, both these

samples show significant higher intensity than L4, prepared without flux.

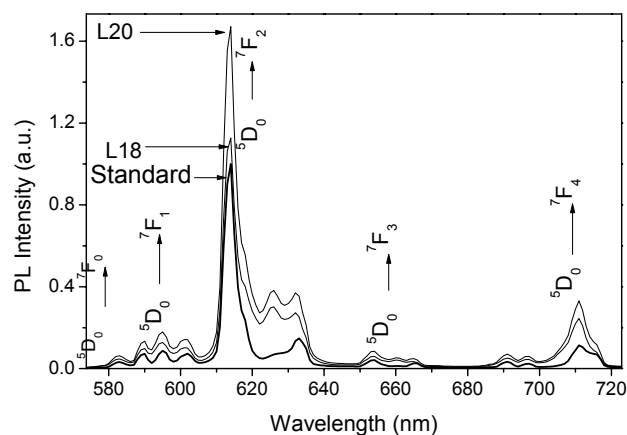


Figure 1. Emission spectra of samples synthesized with sodium tetraborate as flux (L20 and L19) in comparison with the standard

The weak peak at 581 nm (Fig.2) confirms that in our samples Eu^{3+} ions are situated in two crystallographically different lattice sites, which possess C_2 and S_6 point symmetries, respectively.

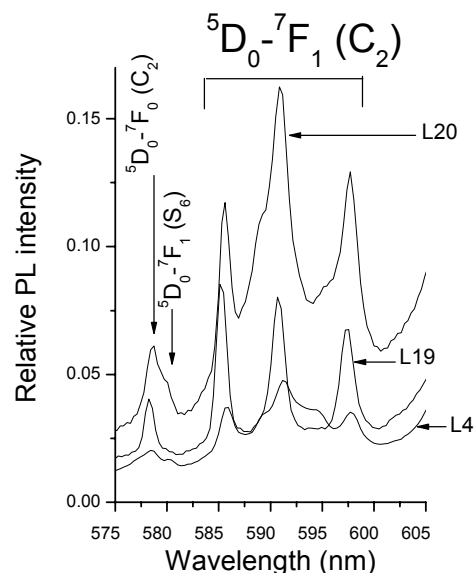


Figure 2. Details of the emission spectra of some $\text{Y}_2\text{O}_3:\text{Eu}$ samples prepared in different synthesis conditions (He-Cd laser excitation with 325 nm; 15 K)

The 7F_2 level of europium is splitted in the host lattice of Y_2O_3 . The behavior of the 610-630 nm band strongly depends on the excitation energy and applied flux. Some peaks 612, 615, 622 and 630 nm near the main peak 609 may be observed for L20 sample. At high excitation energy (CL for example) certain peaks disappeared.

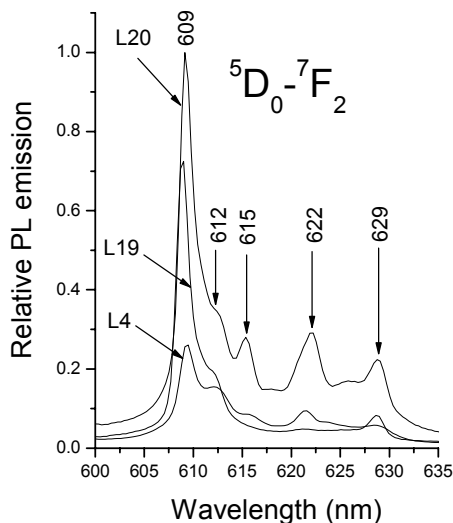


Figure 3. Details of low temperature (15 K) emission spectra of $Y_2O_3:Eu$ (10%) for samples prepared without flux (L4) and with $Na_2B_4O_7$ (L20) or $BaCl_2$ (L19) as flux.

In general, the activator ions incorporated into the host-lattice crystal, can be optically excited in the three ways via their absorption bands: 1) direct excitation into the ions absorption band; 2) excitation into associated activator-host absorption (i.e. charge transfer band, CTB), and 3) indirect excitation via absorption of host-lattice, i.e. radiative recombination of mobile electron-hole pairs (radiation-induced carriers) at activator ions. The excitation spectra (Fig.4) permitted us to estimate the “magnitude” of charge transfer band and as a result, to propose a relaxation model (Fig.5). Between 325 and 380 nm, the direct excitation of europium 5D levels could be observed whereas, in the 210–300 nm range, the excitation via $Eu^{3+}-O^{2-}$ charge transfer (CT) state is dominant. The intensity of CT excitation is significantly dependent on the activator concentration and flux.

When a deep-ultraviolet (254 nm) photon is absorbed by Eu^{3+} , the Eu^{3+} is excited into a charge transfer band. For isolated Eu^{3+} ions (those incapable

of transferring energy to another species in the phosphor lattice), the excitation relaxes sequentially through the various energy states of the ion, quickly to the 5D_3 level, then more slowly, but still sequentially through the 5D levels to the 5D_0 level, which has a high probability of emitting a photon.

At higher excitation energy (CL, for example), the effect of sodium tetraborate is not so efficient, when CT state and host lattice play a dominant role. By exciting Eu^{3+} activators with ultraviolet photons at 365 nm all absorption is in upper F-levels and role of flux is more important.

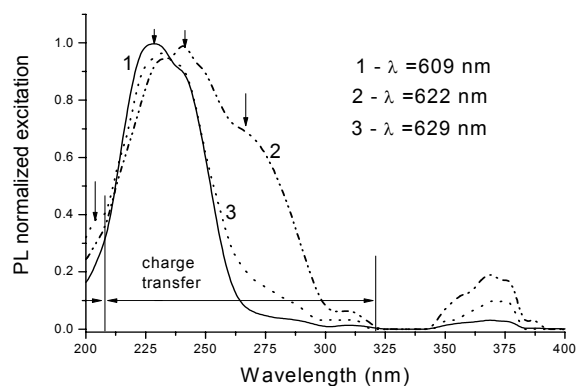


Figure 4. Excitation spectra of ${}^5D_0-{}^7F_2$ emission band for the L18 sample

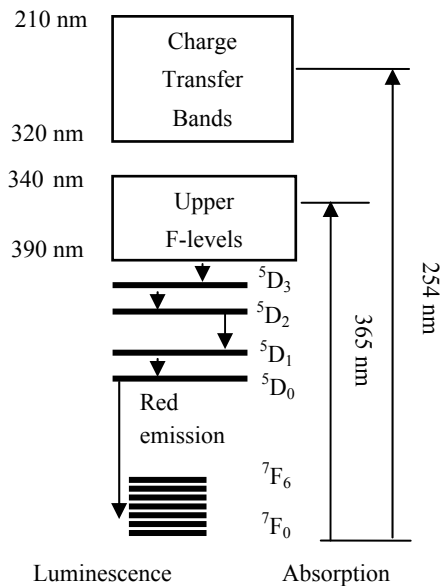


Figure 5. Energy levels for Eu^{3+} and relaxation model

4. Conclusion

The direct correlation between synthesis conditions, such as activator concentration, annealing temperature or flux and luminescence properties was established.

Light-emitting output of samples prepared with barium chloride and sodium tetraborate as flux exceeded the commercial ones by 20-30 %.

The aforementioned results confirm that europium doped yttrium oxide prepared in the presence of barium chloride and sodium tetraborate as flux are perspectives for PL and CL applications.

5. Acknowledgements

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Table 1. The sample code and the relative intensity (in brackets) for Y₂O₃:Eu phosphor under PL 365 nm excitation

Activator concentration	Temperature 1100 ^o C		Temperature 1300 ^o C				Temperature 1400 ^o C	
	No flux	BaCl ₂ (2%)	No flux	BaCl ₂ (2%)	BaCl ₂ (5%)	Na ₂ B ₄ O ₇ (5%)	No flux	BaCl ₂ (2%)
2% mol Eu			L1 (7)	L5 (13)	L13 (15)	L14 (26)		
6% mol Eu			L2 (20)	L6 (36)	L15 (61)	L16 (71)		
10% mol Eu	L9 (6)	L10 (13)	L3 (29)	L7 (60)	L17 (96)	L18 (120)	L11(41)	L12 (104)
15% mol Eu			L4 (46)	L8 (85)	L19 (137)	L20 (176)		