

**SYNTHESIS AND LUMINESCENT PERFORMANCES OF RED EMITTED
PHOSPHORS IN SYSTEMS $Y_2O_3 - La_2O_3 - Gd_2O_3$, $Y_2O_2S - La_2O_2S - Gd_2O_2S$ AND
 $YVO_4 - GdVO_4$ DOPED BY Eu^{3+}**

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ABSTRACT

Phosphors based on solid solutions of $Y_2O_3 - La_2O_3 - Gd_2O_3$ and $Y_2O_2S - La_2O_2S - Gd_2O_2S$ and $YVO_4 - GdVO_4$ doped by Eu^{3+} were synthesized by different methods. Influence of synthesis conditions, composition of the matrix and activator concentration on light-emitting performances of the phosphors is described. Various experimental methods are applied to better understand the influence of synthesis parameters on luminescent properties. Optimized synthesis conditions are proposed. The solid solutions $Y_2O_3 - La_2O_3 - Gd_2O_3$ and $Y_2O_2S - La_2O_2S - Gd_2O_2S$ are formed at temperatures of the phosphor synthesis. Europium-doped Y, La, Gd oxysulphides phosphors show higher CL efficiency at low applied voltages than oxides ones. The presented results confirm that europium doped solid solutions of Y-Ga-La oxides, oxysulphides and vanadates are perspective for PL and CL application.

INTRODUCTION

Oxides, oxysulphides and vanadates of some rare-earth elements (REE) /Y, La, Gd/, doped with Eu^{3+} are widely used to provide red emission for modern display devices. Recently, flat panel displays (FPDs) such as plasma display panels (PDPs), field emission displays (FEDs) and liquid crystal displays (LCDs) have much attention because they can be made in light weight, thin thickness and large screen size. The phosphor materials are of important parts in the FPDs because they directly influence the brightness and the lifetime. So, much attention is given to design and preparation of high efficient phosphor materials. The phosphors used for practical applications must have high luminescence efficiency, high resistance to current saturation, good chromaticity and chemical/thermal stability. For practical application of phosphors it is desirable to have a fine particle size for high resolution and chemical purity for optimum chromaticity and brightness. When employing high excitation voltages (>5 kV), the phosphors used for cathode ray tubes (CRTs) can be used in FEDs and PDPs. However, the efficiency of these phosphors optimized for CRTs drops rapidly as the excitation voltage is lowered below 4 kV. The decreased efficiency is thought to be a result of the reduction in the electron penetration depth as the excitation potential is decreased. Low voltage FEDs and PDPs require the development of phosphors that are bright and efficient under low energy excitation, are stable at high currents, and have good saturation

characteristics. Great efforts have been put into developing the low voltage phosphors, which are efficient and stable. The phosphors proposed and investigated in present paper effectively convert excitation energy into visual light and show high chemical and radiation stability. The energy of excitation is absorbed mainly by the phosphor matrix, because the concentration of the activator ions is low (usually less than 10 wt %). Thus, the requirement to the matrix composition becomes very important. [1-3].

Such REE oxides as Y_2O_3 , La_2O_3 , Lu_2O_3 , are suitable for phosphor matrices because their cations have no unpaired electrons in their electronic configurations and their total orbital and spin moments are equal to zero. They are transparent for visual light, have no low-energy levels and interaction between the REE activator ions and the matrix is minimal in these oxides. Gd_2O_3 is close to the aforementioned oxides according to their optical properties.

Other promising matrices for phosphor application are REE oxysulphides, such as Y_2O_2S , La_2O_2S , Gd_2O_2S , and Lu_2O_2S [4-7]. They form isostructural series crystallizing in the trigonal singony, which is commonly represented in the hexagonal aspect with a local symmetry of the C_{3v} lanthanide site [8].

Red-emitting $YVO_4:Eu$ as the first rare earth activated phosphor was introduced by L. G. Van Uitert et al in 1962 [9]. Nowadays this composition is widely used as the red component in CRT and recently is also being considered as a promising candidate for PDPs due to its good color purity [10].

The isomorphic substitution of yttrium with some REE (e.g., Ln and Gd) in oxides, oxysulphides and vanadates changes their luminescent efficiency.

The aim of the present work is to reveal influence of synthesis conditions and composition of the matrix in the system $Y_2O_3 - La_2O_3 - Gd_2O_3$, $Y_2O_2S - La_2O_2S - Gd_2O_2S$ and $YVO_4 - GdVO_4$ on their light-emitting performances and optimize the synthesis conditions and parameters.

EXPERIMENTAL DETAILS

A. CHEMICAL SYNTHESIS.

The luminance properties, as well as morpho-structural characteristics, strongly depend on phosphors synthesis conditions. In the present work the polycrystalline samples were prepared both by coprecipitation methods (PM) and solid-state reaction (SSR). The investigated phosphors were synthesized from Y, Gd, La oxides and their solid solutions by the following methods:

Coprecipitation of Y, Gd, and La oxalates with their subsequent annealing in air.

REE oxides were taken in equimolar ratios and dissolved in nitric acid ($\rho = 1.2 \text{ g/cm}^3$). The activator was introduced as europium nitrate. Its content was ranged from 2.5 to 10 mol % of an europium oxide. The pH of the solution was brought to 2.0 by adding of an ammonia solution. Then a saturated solution of oxalic acid was added till complete coprecipitation of Y, Gd, and La oxalates occurred. The precipitates were filtered, washed with distilled water, and dried in air at 80°C during 6 hours. The blends were placed into quartz crucibles and annealed in air at 1100°C during 12 hours. After the annealing, the blends were quenched in air at room temperature.

Coprecipitation of Y, Gd, and La oxalates and their annealing in air with melt.

Like in the first method, the oxides were dissolved in a nitric acid; the activator was added, with subsequent coprecipitation of oxalates. The Na_2CO_3 melt was added to the

oxalates blend in fivefold concentration to the blend mass. It allows reducing the annealing temperature to 900°C and the annealing time to 6 hours. After the annealing, the samples were quenched in air, rubbed, and washed out from the melt by distilled water. Then the samples were dried at 80-100°C in air during 4-5 hours. This method allows reducing the synthesis temperature, but it is not so effective due to lower issue of the final product and its enhanced contamination.

Synthesis of phosphors from europium-doped Y, La, Gd oxysulphides and their solid solutions.

Solid solutions of Y, Gd, and La oxysulphides were synthesized by coprecipitation of oxalates with subsequent thermal decomposition. For synthesis of the blend, the solutions of the equimolar amounts of the REE oxides in nitric acid ($\rho = 1.2 \text{ g/cm}^3$) or saturated solution of oxalic acid were used. The REE oxalate precipitate was filtered and dried at 90°C for 2 hours. The stoichiometric amounts of sodium carbonate, sodium phosphate ($\times 12\text{H}_2\text{O}$), and a threefold excess of sulphur were added to the dried precipitate. The blend was wetted with ethyl alcohol to gruel consistency and dried at permanent mixing till full free-flowing. The dry blend was placed into quartz ampoules for annealing in a reducing atmosphere or vacuum ($< 5 \times 10^{-3}$ Torr). The annealing was carried out within 800 - 1100°C during 1 - 8 hours. After that, the phosphors were cooled, powdered, washed off on a blue-band filter with distilled water, then with 0.01 M hydrochloric acid, and with distilled water again till neutral reaction of the waste water. The phosphors were dried in air in an oven at 80 - 100°C during 2 hours.

The compositions of the investigated systems are presented in Table 1.

Table 1. Composition (mol. %) of the synthesized two- and three-component systems of Y, Gd, and La oxysulphides

Y ₂ O ₂ S	Gd ₂ O ₂ S	La ₂ O ₂ S
10 — 90	—	90 — 10
10 — 90	90 — 10	—
—	10 — 50	990 — 50
34	33	33
50	25	25
60	20	20
70	15	15
80	10	10

Synthesis of (Y_x, Gd_{1-x})VO₄:Eu phosphor by coprecipitation with subsequent annealing in air.

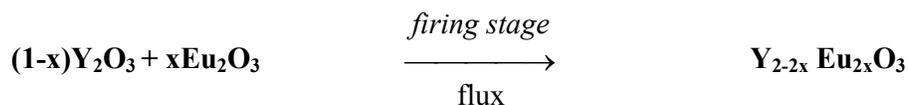
Nanosize powder of Y_{0.95}VO₄:Eu_{0.05} phosphor was prepared by coprecipitation method suggested by R. C. Ropp in 1971 [11]. For this aim, three solutions were prepared. In solution A, Y₂O₃ and Eu₂O₃ were taken in equimolar ratios and dissolved in nitric acid (30%). In solution B, V₂O₅ was dissolved in nitric acid (30%) separately because vanadium exists as a form vanadium radical VO²⁺ in nitric solution. Subsequently solutions A and B were diluted with distilled water, respectively, and solution C is a mixture of NH₄OH and H₂O₂ with 3:1 ratio. Finally, a diluted solution A was added to a diluted solution B and pH of the resulting mixture was brought to 8.0 by adding of the solution C. The final mixture was stirred and heated to about 80 °C until the precipitation takes place. Overall process is explained by the following reaction:



The precipitates were washed with distilled water, filtered, dried in trays with a large exposed surface area, and fired in air during 2 hours at 1100 ~ 1400 °C. Samples of YVO₄:Eu and (Y_X, Gd_{1-X})VO₄:Eu (X = 0 ~ 1.0) were also prepared by solid-state reaction.

Synthesis of Y₂O₃:Eu by ceramic techniques and homogeneous precipitation route

This paper is the first in a series referring to Y₂O₃:Eu synthesis by both ceramic techniques (similar to SSR) and homogeneous precipitation route and is aiming at illustrating the correlation between PL and CL characteristics and the synthesis conditions. Polycrystalline phosphor samples were prepared by thermal synthesis at 1100-1400°C, from homogeneous mixtures containing yttrium oxide (host lattice), Eu₂O₃ (activator source) and alkaline earth salts (flux). Polycrystalline phosphor samples were prepared by thermal synthesis from homogeneous mixtures containing yttrium oxide (p.a. Merck) as host lattice, Eu₂O₃ (Merck) as activator source and luminescent grade BaCl₂ and borax as flux. Phosphors were fired for 2 hrs, in air (un-closed system), at 1100-1400°C; the as-prepared material was washed, dried and sieved. Phosphor synthesis was performed by firing homogeneous and well defined mixtures of yttrium oxides, europium oxide and barium chloride or borax. Phosphor synthesis conditions and some of their general properties are presented in Table 2. The phosphor formation could be described by the equation



B. STRUCTURAL CHARACTERIZATION.

Phosphor samples were characterized by crystalline structure and luminescent properties. Particle sizes and morphologies of the investigated phosphors were determined by scanning electron microscope (SEM) -XL30SFEG. To control the particle size and to find the size distribution the Laser diffraction was carried out using HELOS particle size analysis system. The volume and surface particle distributions were found and compared.

Crystal structures of the prepared samples were characterized by X-ray diffraction using a X-ray diffractometer D/max – RC, Rigaku, Japan with Cu K α radiation (λ = 1.54056 Å)

C. LUMINESCENT CHARACTERIZATION.

Photoluminescence (PL) and cathodoluminescence (CL) measurements put in evidence the influence of thermal synthesis conditions on REE incorporation degree into the host lattice.

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 Photoluminescence System (Professional Scientific Instrument Co, Korea). The excitation was performed with a 254 nm UV radiation as well as 365 nm. To explain the energy transfer VUV excitation (λ =147 nm) was also used.

Low voltage CL was measured at the excitation energy of 0.5-1 keV with the beam current density of 100 μ A/cm² by using a Kimball Physics FRA2X-2/EGPS-2X1 electron gun system. The e-gun system was installed in a demountable ultrahigh-vacuum chamber equipped with a CL spectrophotometer. Vacuum level of 1 \times 10⁻⁷ Torr was maintained during the measurements.

High voltage local CL measurements were performed with a special CL spectrometer, combined with a standard “Camebax” [12]. CL emission was excited with electron beam with diameter up to 1 μm and energy of 5- 40 keV. In these conditions, the electron current that reaches the sample surface could vary from 0.01 to 100 nA and the excitation density, from 10^{-2} to 10^3 W/ m^2 .

Express-analysis of luminescence topographic distribution was carried out with a modified SEM “Stereoscan” with an additional special attachment for colour CL (CCL) [13]. We used both monochromatic and panchromatic CCL-SEM modes. At the monochromatic mode the CL emission was detected at a definite wavelength. At the panchromatic CL-mode the CL was recorded at all the visible emission wavelengths. By this way, the monochromatic CL corresponds to definite transitions between the defect levels of the activator. Spatial distribution of the monochromatic or panchromatic CL on the surface under study was recorded in forms of corresponding CCL-maps. A variety of colours observed in panchromatic CCL-map shows, therefore, a spatial distribution of all the luminescent centres that occurred by nature or design on the surface of investigated phosphors. It has been shown that the use of colour contrast increases the information content of colour image in comparison with its black-and-white counterpart by about two orders of magnitude [13].

RESULTS AND DISCUSSION

Y₂O₃:Eu phosphor.

From the SEM images it is clearly seen that the powders consist of fine particles of mainly 200-300 nm in diameter, but sometimes up to 1 μm and more (Fig.1).

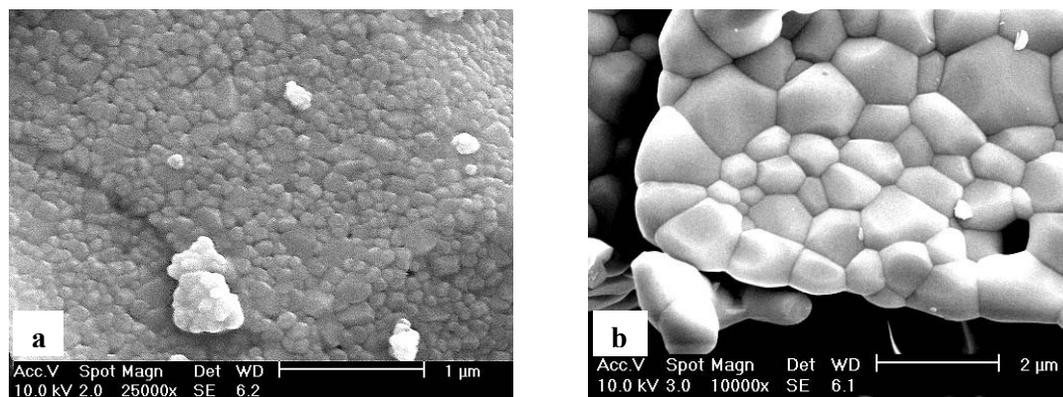


Fig.1. SEM micrographs of some samples Y₂O₃:Eu L17(a) and L20 (b) prepared in different conditions

The particle sizes strongly depend on the synthesis methods and synthesis conditions. To analyse this phenomenon the distribution of particles sizes on the surface and in the volume was carried out using the Laser diffraction method. Some results for several marked investigated phosphors are presented in Figs.2, 3.

As we can conclude from comparison of SEM images and particle size distribution, not only the single particles, but their agglomerates with linear dimensions of about 10 μm are also presented on the surface.

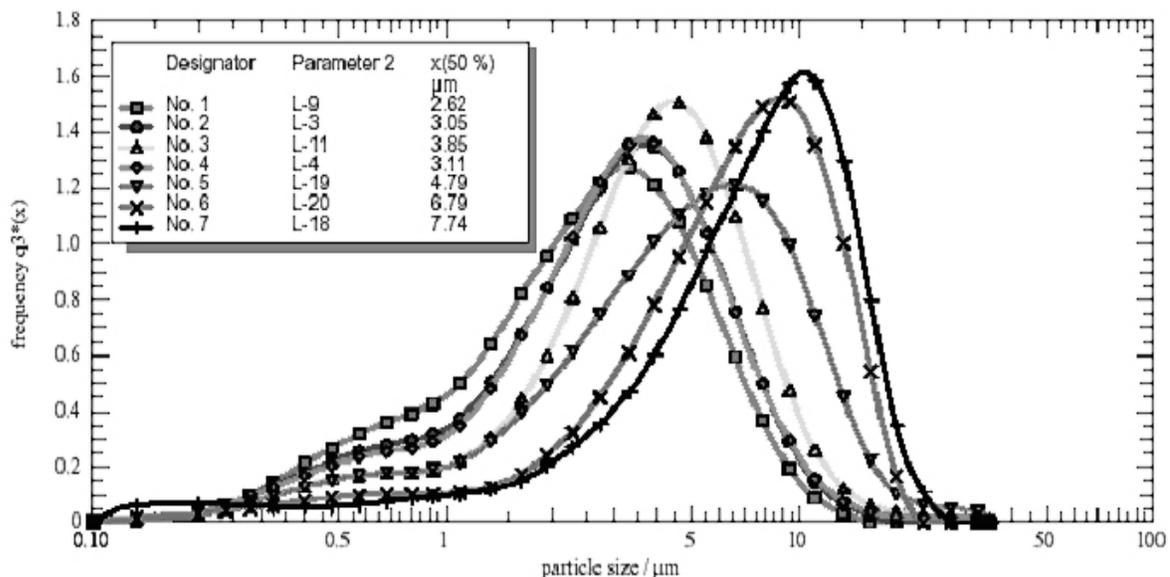


Fig.2. Surface particle size distribution for some of investigated $Y_2O_3:Eu$ phosphors

The crystallite size distribution is a narrow Gaussian type curve with maximum at about 0.2-0.4 μm for different samples (Fig.3). The shape of the lattice strain distribution curve suggests that the sample is perfectly crystallized.

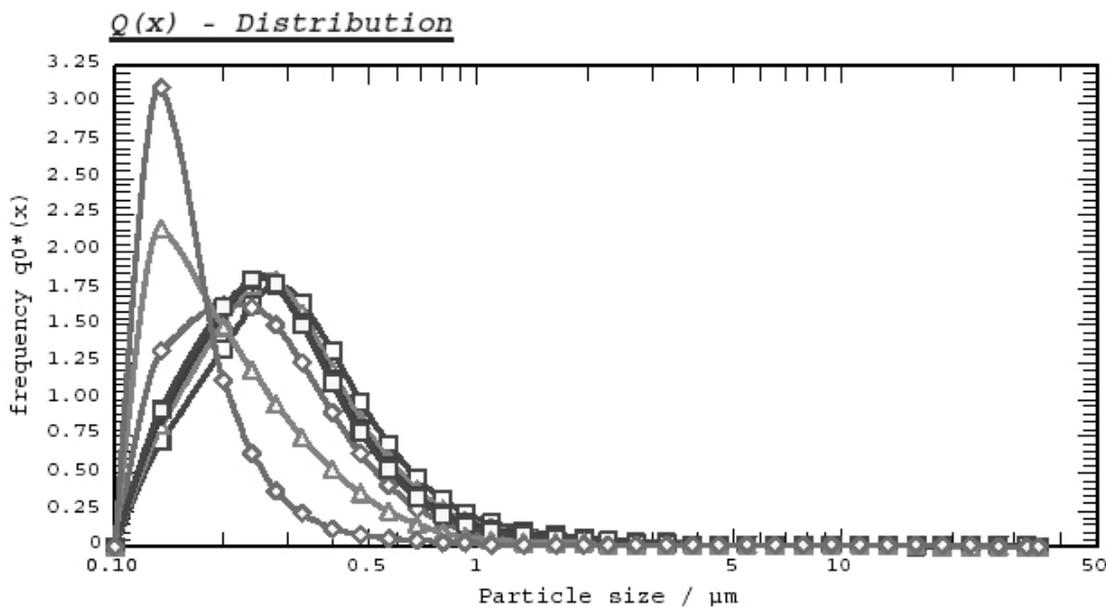


Fig.3. Calculated particle size distribution in the volume for the same phosphors as in Fig.2

Under UV and electron beam excitations, europium activated yttrium oxide phosphor shows bright characteristic red luminescence. CL results and PL emission and excitation spectra of the samples are shown in Figs.4-8.

Our experimental technique allows us to observe the following Eu-emission bands: ~

460 nm band, in the blue part of the spectrum, and 589, 611, 650, and 710 nm bands, in the red spectral domain. The main peak position and its relative intensity (I_{\max}) are shown in Table 2.

Table 2. General properties of some phosphor samples prepared in various conditions.

Code	Phosphor formula	Article I. Synthesis conditions			PL colour	PL characteristics at $\lambda_{\text{exc}}=365$ nm	
		Europium (mol %)	Flux	Firing temperature		λ_{\max} (nm)	I_{\max} (%)
Section 1	$\text{Y}_{1.990}\text{Eu}_{0.010}\text{O}_3$	1.0	-	1300 ⁰ C	pink	608.4	19
L2	$\text{Y}_{1.970}\text{Eu}_{0.030}\text{O}_3$	3.0	-	1300 ⁰ C	reddish	610.0	25
L3	$\text{Y}_{1.950}\text{Eu}_{0.050}\text{O}_3$	5.0	-	1300 ⁰ C	reddish	611.7	35
L4	$\text{Y}_{1.925}\text{Eu}_{0.075}\text{O}_3$	7.5	-	1300 ⁰ C	red	611.7	46
L5	$\text{Y}_{1.990}\text{Eu}_{0.010}\text{O}_3$	1.0	BaCl ₂ (2%)	1300 ⁰ C	reddish	610.6	27
L6	$\text{Y}_{1.970}\text{Eu}_{0.030}\text{O}_3$	3.0	BaCl ₂ (2%)	1300 ⁰ C	red	610.0	48
L7	$\text{Y}_{1.950}\text{Eu}_{0.050}\text{O}_3$	5.0	BaCl ₂ (2%)	1300 ⁰ C	red	610.6	58
L8	$\text{Y}_{1.925}\text{Eu}_{0.075}\text{O}_3$	7.5	BaCl ₂ (2%)	1300 ⁰ C	red	610.6	88
L9	$\text{Y}_{1.950}\text{Eu}_{0.050}\text{O}_3$	5.0	-	1100 ⁰ C	pink	608.4	15
L10	$\text{Y}_{1.950}\text{Eu}_{0.050}\text{O}_3$	5.0	BaCl ₂ (2%)	1100 ⁰ C	pink	609.5	18
L11	$\text{Y}_{1.950}\text{Eu}_{0.050}\text{O}_3$	5.0	-	1400 ⁰ C	red	610.6	48
L12	$\text{Y}_{1.950}\text{Eu}_{0.050}\text{O}_3$	5.0	BaCl ₂ (2%)	1400 ⁰ C	red	610.6	98
L13	$\text{Y}_{1.990}\text{Eu}_{0.010}\text{O}_3$	1.0	BaCl ₂ (5%)	1300 ⁰ C	pink	611.3	30
L14	$\text{Y}_{1.990}\text{Eu}_{0.010}\text{O}_3$	1.0	Borax (5%)	1300 ⁰ C	pink	611.2	33
L15	$\text{Y}_{1.970}\text{Eu}_{0.030}\text{O}_3$	3.0	BaCl ₂ (5%)	1300 ⁰ C	red	611.2	62
L16	$\text{Y}_{1.970}\text{Eu}_{0.030}\text{O}_3$	3.0	Borax (5%)	1300 ⁰ C	red	611.5	80
L17	$\text{Y}_{1.950}\text{Eu}_{0.050}\text{O}_3$	5.0	BaCl ₂ (5%)	1300 ⁰ C	red	611.2	78
L18	$\text{Y}_{1.950}\text{Eu}_{0.050}\text{O}_3$	5.0	Borax (5%)	1300 ⁰ C	red	611.0	110
L19	$\text{Y}_{1.925}\text{Eu}_{0.075}\text{O}_3$	7.5	BaCl ₂ (5%)	1300 ⁰ C	red	610.6	130
L20	$\text{Y}_{1.925}\text{Eu}_{0.075}\text{O}_3$	7.5	Borax (5%)	1300 ⁰ C	red	611.7	155
	STANDARD	-	-	-	RED	610.6	100.0

Excitation spectra show that the 611 nm emission band is well excited in the UV-VIS region. Three mechanisms govern the absorption in $\text{Y}_2\text{O}_3:\text{Eu}$: direct excitation of the Eu^{3+} ion, excitation via a charge-transfer state between the Eu ion and neighbouring O ions, or excitation via the Y_2O_3 host lattice.

Eu-specific luminescence (the red domain bands) is the result of some ${}^5D_0 \rightarrow {}^7F_J$ electronic transitions inside the activator ion. Position of the spectra and relative intensity depend on the activator incorporation degree (AID) into the Y_2O_3 host lattice and this one is strongly influenced by the flux presence (Figs.6-8).

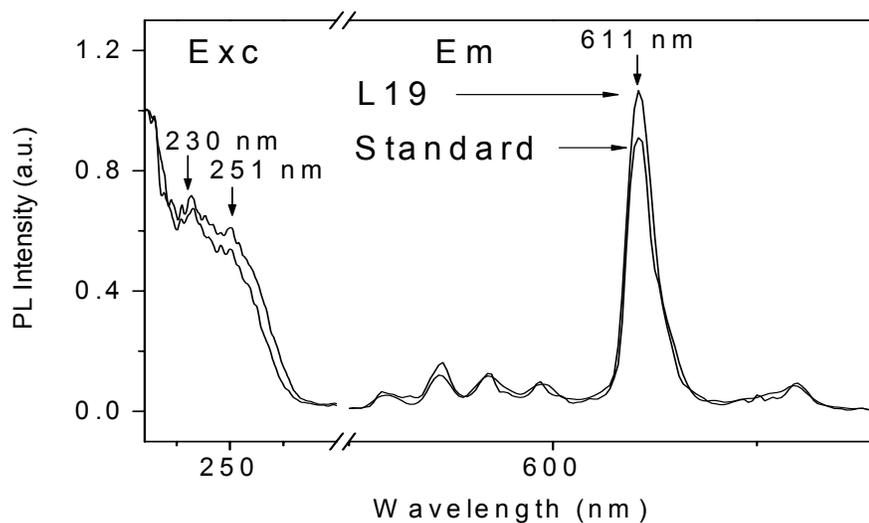


Fig 4. Emission and excitation spectra of L19-sample [7.5 mol% Eu; 5% BaCl₂ 1300°C] in comparison with Standard sample

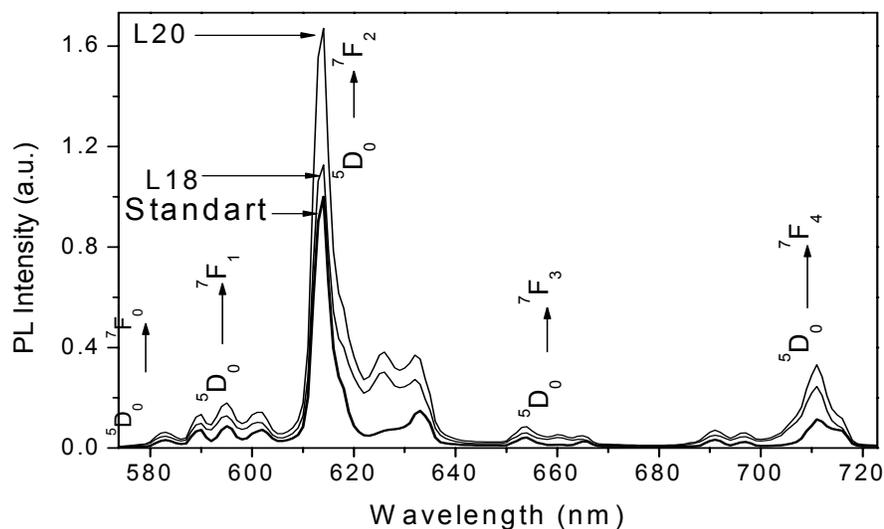


Fig 5. Emission spectra excited by 365 nm of some Y₂O₃: Eu samples: L18 [5 mol % Eu; 5% Borax] and L20 [7.5 mol % Eu; 5% Borax] in comparison with Standard phosphor and the main energy transitions in the red region.

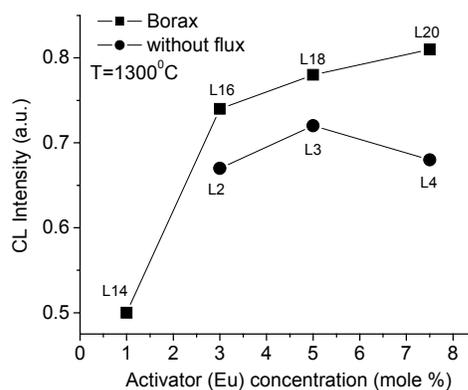
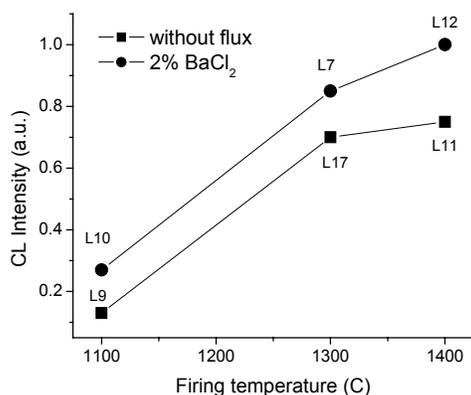


Fig.6. Dependence of CL intensity on firing temperature and flux

Fig. 7. Dependence of CL intensity on activator concentration and flux

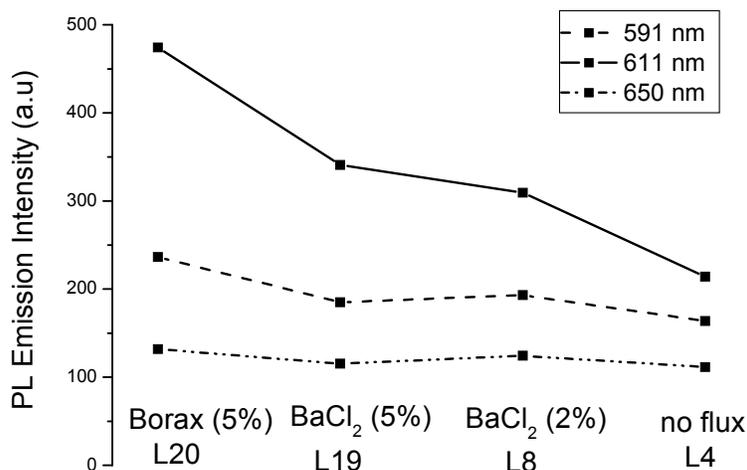


Fig 8. Dependence of the Eu- emission bands PL intensity (365 nm) on flux nature and concentration- phosphor samples L20; L19; L8 and L4 \leftrightarrow Y₂O₃:Eu (7.5 mol %)

The preparation conditions, i.e. quality of the host lattice generating material, activator amount, choice of the mineralizing agent and its concentration, firing conditions influence characteristics of Y₂O₃:Eu phosphor.

The activator incorporation degree depends on phosphor synthesis conditions. The specific emission band of L1-L20 samples is disposed between 608.4 and 611.7 nm whereas the relative emission intensity varies from 15 % to 155 %.

Colour Cathodoluminescence - Scanning Electronic Microscopy (CCL-SEM) images are very illustrative for the specific luminescence colour of the Y₂O₃: Eu powders. CCL-SEM photos illustrate the effect of firing temperature on the chromatic hue of powder surfaces. From CCL-SEM maps one can conclude that the higher the temperature, the more saturated the red colour.

PL spectra and CL measurements put in evidence the influence of thermal synthesis conditions on Eu- incorporation degree into the yttrium oxide host lattice.

Presence of mineralizing agent as well as the high firing temperature facilitates the formation of the cubic $Y_2O_3 - Eu_2O_3$ solid solution and consequently an efficient activator distribution. The highest AID seems to be attained at $1300^\circ C$ in the presence of 5% borax. The very high PL brightness of the sample is due to its very high excitability, especially in the ~ 398 band. The optimal activator concentration in this synthesis method is 7.5 mol%.

Phosphors in the system $Y_2O_3 - La_2O_3 - Gd_2O_3$ doped by Eu.

Y_2O_3 , Gd_2O_3 , and Eu_2O_3 crystallize in cubic (C) modification and form together continuous series of solid solutions of substitution. Lanthanum oxide crystallizes in hexagonal (H) modification but passes into the monoclinic (M) one after dissolution in yttrium and gadolinium oxides. The crystal structure of $Y_2O_3 - La_2O_3 - Gd_2O_3$ solid solutions is unknown. The ion radius of the La^{3+} (0.117 nm) significantly differs from those of the Y^{3+} , Eu^{3+} , and Gd^{3+} (0.104, 0.108, and 0.109 nm, respectively).

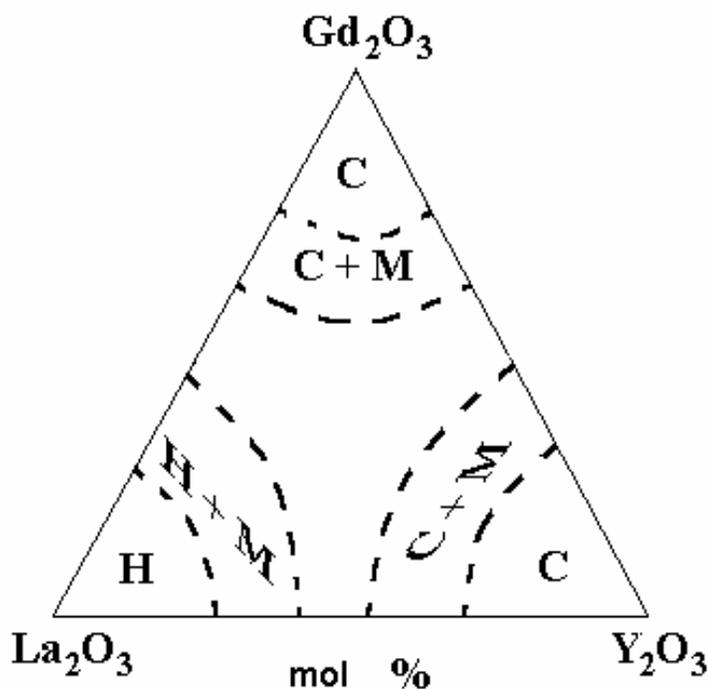


Fig.9. Explored composition range of the solid solutions (C, H, M are the cubic, hexagonal, and monoclinic phases, respectively).

According to our data the investigated solid solutions can be formed over the whole composition triangle and crystallize in the cubic, monoclinic, and hexagonal modifications depending on the composition, Fig. 9. The ternary solid solutions in the explored areas of the composition triangle crystallize predominantly in the cubic structure. The fraction of the hexagonal modification is increased with increase of concentration of lanthanum oxide. The hexagonal and monoclinic phases of solid solutions are formed only in La_2O_3 -rich blends. The

pure hexagonal phase with no impurities was obtained only for the solid solutions containing more than 90 mol % of La_2O_3 . The free monoclinic phase was not isolated at our synthesis conditions. The introduction of an activator (Eu^{3+}) did not influence the crystal structure of the phosphor matrix. Maximum PL intensity (under $\lambda = 394$ nm excitation) of $\text{Y}_2\text{O}_3:\text{Eu}$ and $\text{Gd}_2\text{O}_3:\text{Eu}$ phosphors was achieved at 10 mol % of europium oxide, Fig. 10.

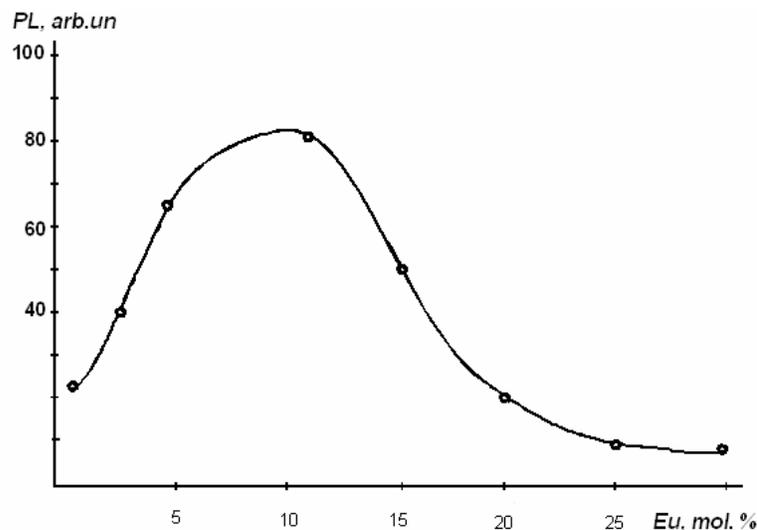


Fig.10. PL intensity of $(\text{Y}_x,\text{La}_{1-x})_2\text{O}_3:\text{Eu}$ phosphor vs. activator concentration.

La_2O_3 increase PL intensity of the solid solutions due to the changes in PL excitation spectra, Fig. 11. The solid solutions of $(\text{Y}_{1-x}\text{La}_x)_2\text{O}_3:\text{Eu}$ show more efficient PL than pure $\text{Y}_2\text{O}_3:\text{Eu}$ at lower energies of exciting photons.

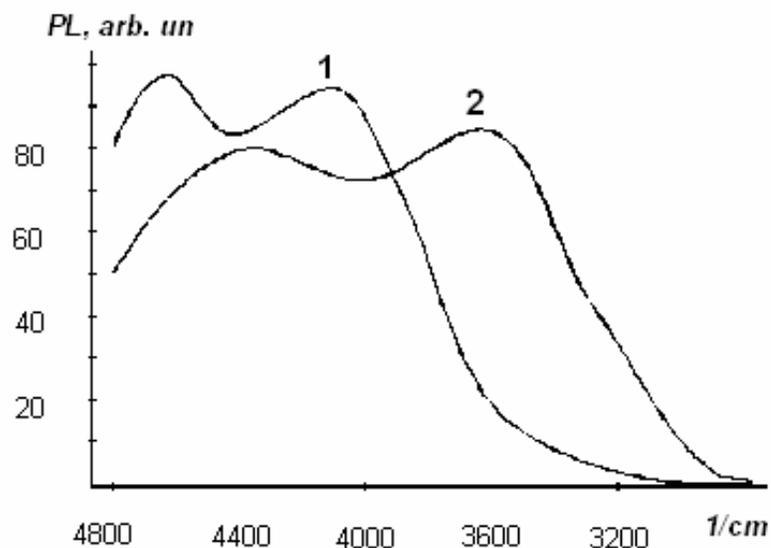


Fig.11. PL excitation spectra of $\text{Y}_2\text{O}_3:\text{Eu}$ (1) and $(\text{Y}_{1-x}\text{La}_x)_2\text{O}_3:\text{Eu}$ (2).

Phosphors in the $\text{Y}_2\text{O}_2\text{S} - \text{La}_2\text{O}_2\text{S} - \text{Gd}_2\text{O}_2\text{S}$ system doped by Eu.

We synthesized series of solid solutions $\text{Y}_2\text{O}_2\text{S} - \text{La}_2\text{O}_2\text{S} - \text{Gd}_2\text{O}_2\text{S}$ possessing either limited or unlimited solubility. The solubility of $\text{La}_2\text{O}_2\text{S}$ in $\text{Y}_2\text{O}_2\text{S}$ achieves 27 mol % at the

annealing temperature of 900 °C, that does not affect the matrix structure. The increase of PL and CL brightness by 20-25 % was achieved after introduction of 20 mol % of La₂O₃ into Y₂O₂S. The formation of a solid solution is accompanied by a shift of the main peaks in the luminescent spectra towards shorter waves, Fig. 12.

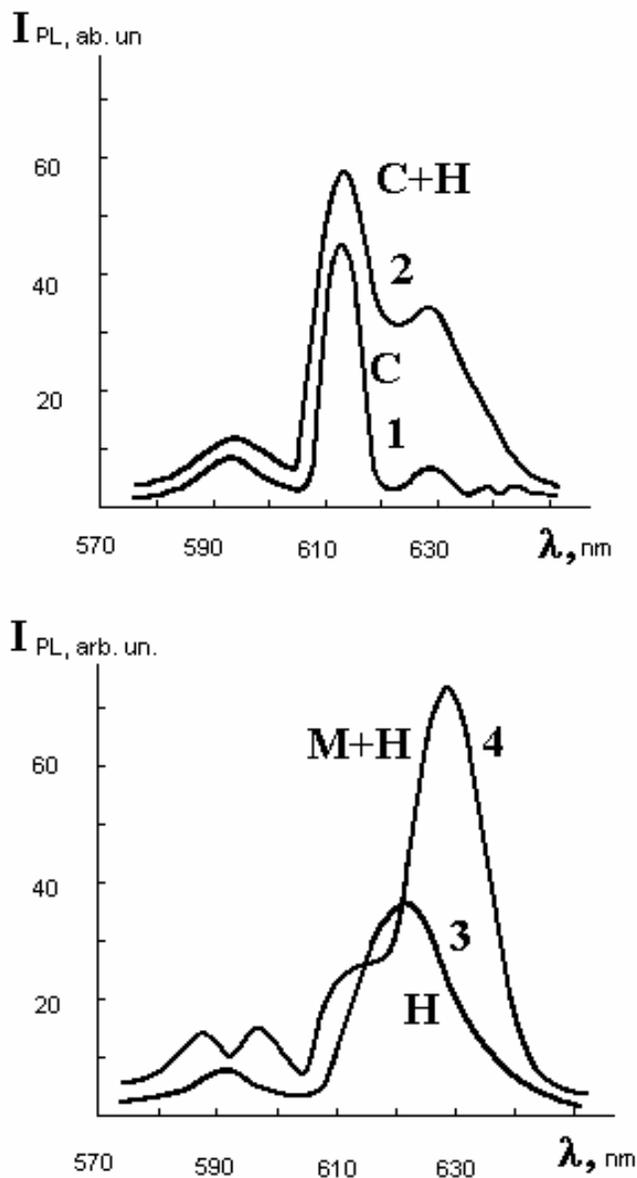


Fig. 12. PL spectra of the following phosphors (the Eu₂O₃ content is 10 mol %):

- (1) 0.70Y₂O₃+0.15Gd₂O₃+0.15La₂O₃;
- (2) 0.60Y₂O₃+0.20Gd₂O₃+0.20La₂O₃;
- (3,4) 0.65La₂O₃+0.175Y₂O₃+0.175Gd₂O₃

The Y₂O₂S-La₂O₂S system shows a limited solubility. The solid solutions with a good crystal structure are formed when the content of Y₂O₂S does not exceed 20 mol % at 900 °C. At higher contents, the crystal structure is saturated by defects and structures are disordered.

When the synthesis temperature is raised up to 1000°C, the solubility is increased to 40 mol %. The same content of Gd₂O₂S can be dissolved in La₂O₂S at a synthesis temperature 1000°C. Unlimited solubility is formed in the Y₂O₂S-Gd₂O₂S system, which can be explained by close values of the ionic radii. This fact also causes almost no shift of the photoluminescence bands over the whole composition range.

Besides binary solid solutions, we synthesized ternary ones of Y, Gd, and La oxysulphides with a predominant content of Y₂O₃. Though the whole composition triangle has not been explored, the solid solutions obtained have a good crystal structure. The introduction of the activator does not affect the matrix structure and luminescent spectra of the phosphor.

This speaks that substitution solutions of RRE of phosphor matrix by activator ion take place. The Y₂O₂S-based solid solutions exhibit the maximum integral intensity among the investigated samples, Table 3.

Table 3. PL intensity of some phosphors vs the matrix composition.

Phosphor	I _{PL} , arb. un.
Y ₂ O ₂ S:Eu	3,87
(Y _{0.3} La _{0.7}) ₂ O ₂ S:Eu	0,90
(Y _{0.75} La _{0.25}) ₂ O ₂ S:Eu	0,70
(Y _{0.6} Gd _{0.4}) ₂ O ₂ S:Eu	2,15
(Y _{0.7} La _{0.15} Gd _{0.15}) ₂ O ₂ S:Eu	0,94
Gd ₂ O ₂ S:Eu	1,95

Phosphors in the YVO₄-GdVO₄ system doped by Eu.

Fig. 13 shows morphologies and particle sizes of YVO₄:Eu phosphor powder prepared by two different methods. As shown in the figure, the particle size of YVO₄:Eu prepared by coprecipitation method was below 200 nm. And it shows narrow particle size distribution, spherical powder and a small degree of agglomeration.

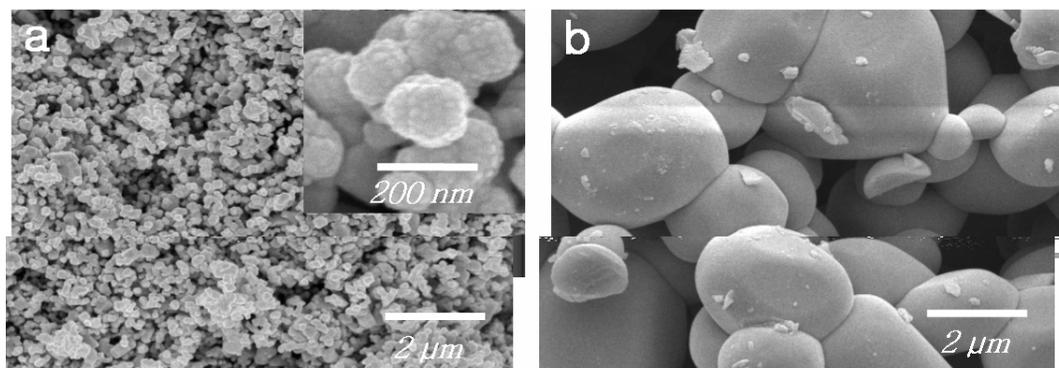


Fig13. SEM micrographs of YVO₄:Eu prepared by (a) PM and (b) SSR

Fig. 14(a) shows X-ray diffraction of nano-sized YVO₄ phosphor obtained just after simple co-precipitation process without heat-treatment. A single and partly crystallized phase was recorded in this case.

An introduction of the activator Eu^{3+} does not influence the crystal structure of the phosphor matrix that was confirmed by XRD analysis. As Fig. 14(b) shows, after subsequent annealing of the samples at $1200\text{ }^\circ\text{C}$ during 2 hours, the crystalline phases of $\text{YVO}_4\text{:Eu}$ and $\text{Y}_8\text{V}_2\text{O}_{17}$ were obtained.

As shown in Fig. 14(c) and 14(d), the phosphors of $\text{YVO}_4\text{:Eu}$ and $(\text{Y}_x, \text{Gd}_{1-x})\text{VO}_4\text{:Eu}$ ($x=0\sim 1.0$) synthesized by solid-state reaction have tetragonal crystal structure with small deviations in lattice constants. The values of the lattice constants of $\text{YVO}_4\text{:Eu}$ and $(\text{Y}_{0.4}, \text{Gd}_{0.6})\text{VO}_4\text{:Eu}$ were estimated as $a = b = 7.112$, $c = 6.29$ and $a = b = 7.178$ and $c = 6.329$, respectively. Since ionic radius of Gd is larger than that of Y the introduction of Gd ion into YVO_4 crystal structure elongates all the three axes. As a result crystal symmetry of YVO_4 was distorted.

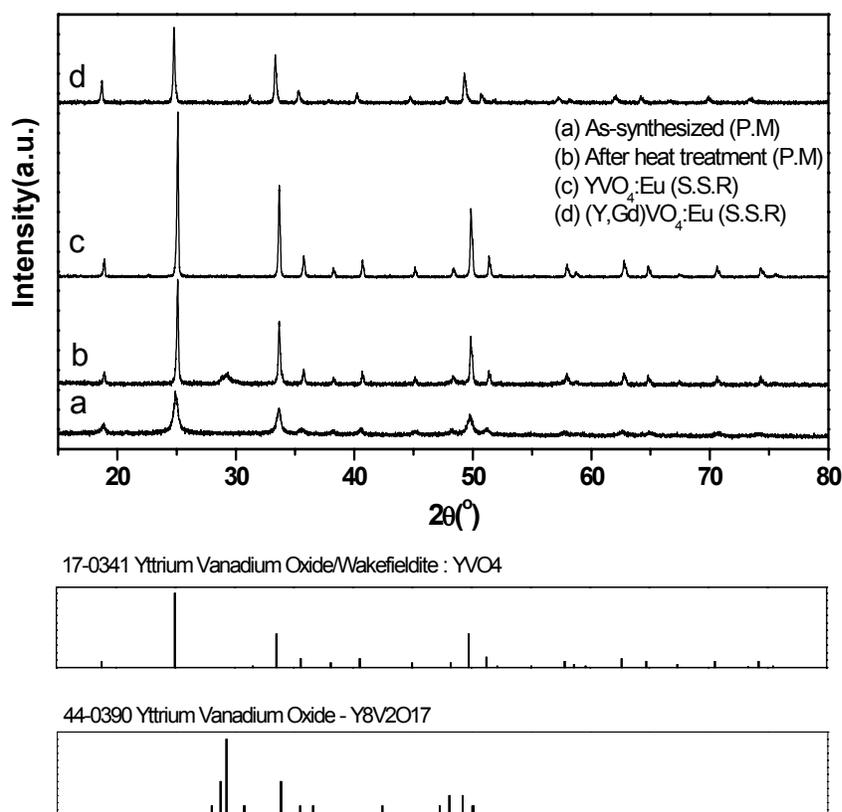


Fig. 14. Powder XRD patterns of (a) As-synthesized $\text{YVO}_4\text{:Eu}$ (PM), (b) $\text{YVO}_4\text{:Eu}$ obtained after heat treatment (PM), (c) $\text{YVO}_4\text{:Eu}$ (SSR), and (d) $(\text{Y}, \text{Gd})\text{VO}_4\text{:Eu}$ (SSR). The 19-0341 and 44-0390 JCPDS files [14] can also be seen to identify the obtained crystalline phases.

Fig. 15 shows spectra of PL excitation and emission of the $\text{YVO}_4\text{:Eu}^{3+}_{0.05}$ phosphor. When Eu replaces Y in non-centrosymmetric site, the very sharp peaks in red region appear instead of broad band blue emission of selfactivated YVO_4 . The emission spectra of $\text{YVO}_4\text{:Eu}^{3+}$ mainly determined by the transitions from the $^5\text{D}_0$ level to the $^7\text{F}_J$ ($J=0,1,2,3,4$) in Eu^{3+} ion. The well known electric dipole transitions are $^5\text{D}_0 \rightarrow ^7\text{F}_2$, which occur when the Eu^{3+} is located in non-centrosymmetric site of the matrix.

The aforementioned results confirm that europium doped solid solutions of Y-Ga-La oxides, oxysulphides and vanadates are perspective for PL and CL application.

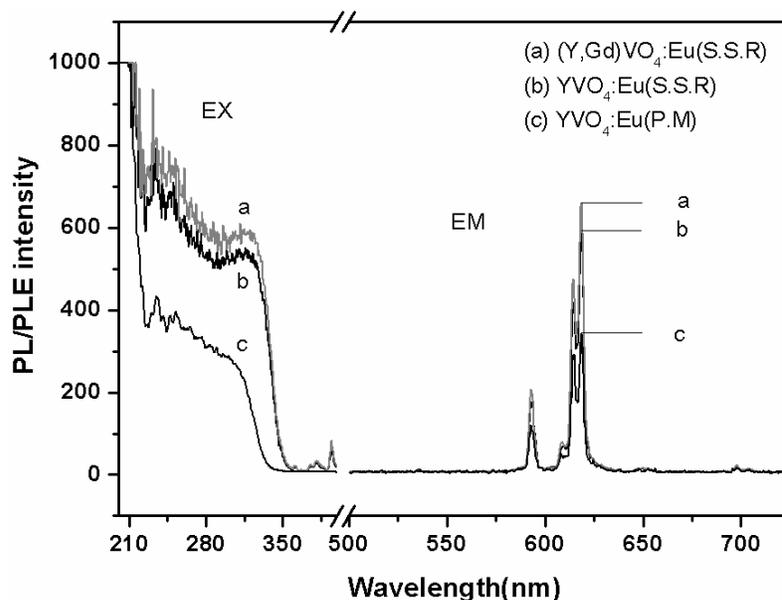


Fig. 15. PL emission and PL excitation spectra of $\text{YVO}_4:\text{Eu}$ phosphor.

CONCLUSIONS

The preparation conditions, i.e. quality of the host lattice generating material, activator amount, mineralizing agent concentration, thermal synthesis conditions and conditioning regime determine the sample characteristics. Some recommendations can be done to optimize the synthesis conditions and improve the luminescent properties.

Presence of mineralizing agent as well as the high firing temperature facilitates the formation of the cubic $\text{Y}_2\text{O}_3 - \text{Eu}_2\text{O}_3$ solid solution and consequently an efficient activator distribution. The highest AID seems to be attained at 1300°C in the presence of 5% borax. The very high PL brightness of the sample is due to its very high excitability, especially in the ~ 398 band. The optimal activator concentration in this synthesis method is 7.5 mol%.

The solid solutions $\text{Y}_2\text{O}_3 - \text{La}_2\text{O}_3 - \text{Gd}_2\text{O}_3$ and $\text{Y}_2\text{O}_2\text{S} - \text{La}_2\text{O}_2\text{S} - \text{Gd}_2\text{O}_2\text{S}$ are formed at temperatures of the phosphor synthesis. Europium-doped Y, La, Gd oxysulphides phosphors show higher CL efficiency at low applied voltages than oxides ones.

The aforementioned results confirm that europium doped solid solutions of Y-Ga-La oxides, oxysulphides and vanadates are perspective for PL and CL application.

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