

Structural and luminescence characterization of yttrium oxide based phosphors prepared by wet- chemical method

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Europium activated yttrium oxide ($Y_2O_3:Eu^{3+}$) phosphor samples were prepared by thermal synthesis, from yttrium-europium precursors prepared by wet chemical synthesis route, using the reagent simultaneous addition technique for precipitation. The thermal treatment of the precursor was performed at 1100-1300°C with various mineralising agents (fluxes) such as: barium chloride, sodium tetraborate, sodium or lithium carbonate alone or in mixture. Phosphor samples were characterised by X-ray diffraction, scanning electronic microscopy, and photoluminescence spectroscopy. It was found that the thermal synthesis regime plays an important role in forming $Y_2O_3:Eu^{3+}$ powders with well defined properties. Photoluminescence performances as well as the micro and macrostructural parameters of phosphor powders are influenced by the flux and the firing temperature used during the thermal synthesis stage.

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1. Introduction

Yttrium oxide doped with europium ($Y_2O_3:Eu^{3+}$) is one of the main red emitting phosphor used in lightning industry and other optoelectronic devices [1-3]. To improve brightness and resolution of displays, it is important to develop phosphors with controlled morphology and small particle sizes. In order to achieve improved luminescent properties of $Y_2O_3:Eu^{3+}$ the precursors characteristics as well as the synthetic route are very important factors.

Many different techniques regarding the preparation of yttrium oxide based phosphors with spherical shape, good crystallinity, high chemical purity, homogeneity and high luminescence efficiency have been reported in the literature, including solid-state reaction [4-6], co-precipitation [7-9], spray pyrolysis [10], hydrothermal [11,12], citrate method [13, 14], sol-gel [15], solvothermal [16], chemical vapor reaction [17], combustion [18,19].

The simultaneous addition technique (SimAdd method) is a wet chemical synthesis route that we used for the preparation of yttrium based precursors with well controlled characteristics and high quality reproducibility. Moreover, the SimAdd method used for precursor preparation enables us to assure a good control for temperature, medium pH, reagents flow, concentration and molar ratio of reactants. Our previous works showed that precursors quality strongly influences the phosphor properties [20-23].

As a result of the previous studies, we present some aspects concerning the thermal synthesis of $Y_2O_3:Eu^{3+}$

powders from yttrium-europium precursors obtained by wet chemical synthesis route, using the reagents simultaneous addition technique *SimAdd*.

It is well known that, for the same host material - activator system, when activator concentration is kept constant, the photoluminescence (PL) characteristics can be correlated with phosphor physical properties such as surface area, particle morphology and sizes, crystallinity, phase purity, activator incorporation degree (AID) [24-29]. Moreover, the activator concentration itself is an important factor that influences the PL properties [30-33].

On the other hand, for the wet chemical synthesis routes, phosphor characteristics are influenced both by precursor quality determined by precipitation conditions (pH, precipitating agent, temperature) and thermal synthesis regime (firing temperature, mineralizing agent, time, atmosphere). For instance, the firing temperature strongly influences the emission intensity due to the effect on the activator distribution and the host-lattice crystallinity. In order to regulate and control the particle size and morphology, different fluxes can be used as mineralizing agents. As a result, synthesis of $Y_2O_3:Eu^{3+}$ powders with predetermined characteristics using the wet chemical route is a complex process that has to take into account a lot of factors, starting with precursor quality and ending with thermal synthesis regime i.e. mineralizing agents and firing temperature.

In this respect the aim of the paper is to study the influence of the thermal synthesis regime on luminescent and morpho-structural properties of $Y_2O_3:Eu^{3+}$ powders

prepared by wet chemical method, using the reagent simultaneous addition technique.

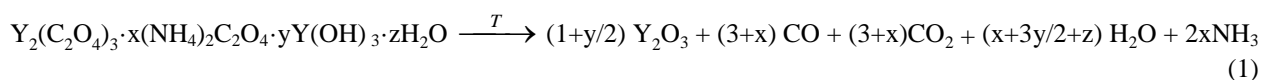
2. Experimental

The preparation of yttrium-europium precursor was achieved by wet chemical method [20-23] which involves a precipitation reaction between the corresponding rare earth nitrates and oxalic acid as precipitant agent. Precipitation was conducted at 80°C, pH=2 and with a molar ratio between rare earth nitrates and oxalic acid of 2:3. Yttrium-europium nitrate solution (0.3M) was added together with oxalic acid (0.45M) into diluted solution of P.R. (1:10). Yttrium- europium ratio was varied between 0.97:0.03 to 0.90:0.10. The precursor post precipitation stage consists in 24 h ageing, washing and drying.

After mixing the precursor with different mineralising agents (BaCl₂, Na₂CO₃, Li₂CO₃, Na₂B₄O₇, Na₄P₂O₇), the synthesis mixtures were thermally treated in air, for 2 hrs, at 1100÷ 1300 °C and carefully conditioned by water wash, drying, and sieving.

Phosphor samples were characterised by *infrared absorption spectroscopy* (JASKO 610 FTIR Spectrometer; KBr pellets technique), *photoluminescence measurements - PL* (JASKO FP-6500 Spectrofluorimeter Wavel; λ_{exc}=254nm), *X-ray diffraction-XRD* (D8Advanced Bruker Diffractometer, CuKα radiation;), *Scanning Electronic Microscopy-SEM* (JEOL -JSM 5510LV Microscope; Au-coated), *BET measurements* (volumetric apparatus for Kr adsorption at liquid nitrogen temperature), and *Chemical Analysis* (ICP Emission Spectrometer BAIRD, after dissolving phosphor samples in nitric acid).

The microcrystalline parameters were determined on the basis of XRD data performed with a DRON-3M powder diffractometer, followed by processing the data by



Different fluxes were used to improve the incorporation of europium into the yttria crystalline lattice, to ameliorate the crystalline order degree of the host lattice, and to regulate the powders particles size (and specific surface area).

The as prepared phosphor powders were investigated in order to establish the morpho-structural and photoluminescence characteristics. Thermal synthesis conditions and some phosphor characteristics such as photoluminescence intensity (I_{em}) and specific surface area (S_σ) are presented in Table 1. PL intensity was determined from the emission spectra (λ_{exc}=254 nm), in comparison with a solid state reaction product considered 100% (Y₂O₃:Eu; Kemira).

PL intensity values of phosphor samples are situated in a relatively wide domain from 50.7% (P28a) to 101.2% (P52k), depending on the thermal synthesis regime.

Warren-Averbach method applied to band-profile (CrysFire program- XRLINE program based).

3. Results and discussion

In order to determine the influence of the thermal synthesis regime on the morpho-structural and photoluminescence characteristics of Y₂O₃: Eu³⁺ phosphor, yttrium-europium precursor was prepared by *SimAdd* technique from mixture containing yttrium nitrate and europium nitrate in variable ratios, and oxalic acid as precipitating reagent. The precursor quality was evaluated on the basis of thermal analysis, FT-IR and XRD measurements and was presented in previous paper [22]. It was found that the thermal decomposition proceeds in two major steps that could be associated with water loss (at ~ 193°C) and decomposition of metallic oxalate (at around ~406°C). FT-IR spectrum contains mainly the characteristic bands for oxalate, namely: ν(C=O) ~1634, ν(C-O) ~1324, δ(O-C=O)+(Y-OH) ~814-790. XRD pattern indicates that precursor contains mainly the crystalline phase of yttrium ammonium oxalate (PDF 221047). All these investigations suggest that yttrium oxalate-based precursor can be described by the general formula Y₂(C₂O₄)₃·x(NH₄)₂C₂O₄·yY(OH)₃·zH₂O; the partial substitution of yttrium with europium is neglected.

After mixing the precursor with different mineralizing agents, the synthesis mixtures were thermally treated at 1100÷ 1400 °C and carefully conditioned.

Thermal treatment of the yttrium-europium precursor assure the complete conversion into europium activated yttrium oxide phosphor, according to the reaction (1). For simplicity, the substitution of 3 mol % yttrium with europium is ignored.

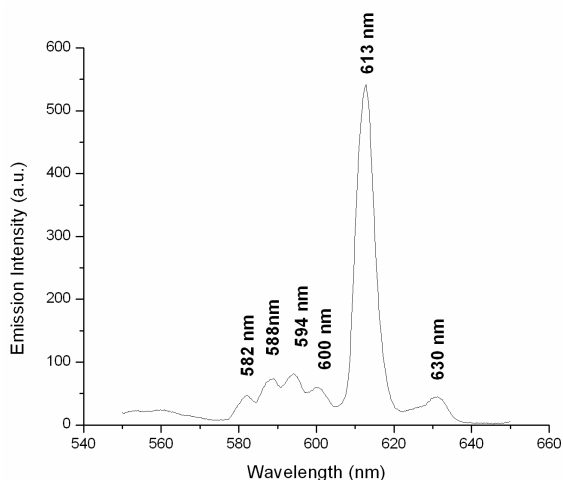
Moreover, the increase of the firing temperature leads to the formation of phosphor powders with larger particle size, as illustrated by the specific surface area values. The presence of Li₂CO₃ as mineralising agent alone or in mixture generates phosphor powders with relatively large particle sizes.

Photoluminescence of red emitting Y₂O₃: Eu³⁺ phosphor was evaluated on the basis of emission and excitation spectra (Figure 1 and Fig. 2). Under 254 nm excitation, the phosphor emits predominantly in the red domain, i.e. at ~ 590 nm (⁵D₀ → ⁷F₁ electronic transition) and ~613 nm (⁵D₀ → ⁷F₂ transition). Phosphors excitation proceeds mainly in the charge transfer band (Eu³⁺ - O²⁻) in the UV domain.

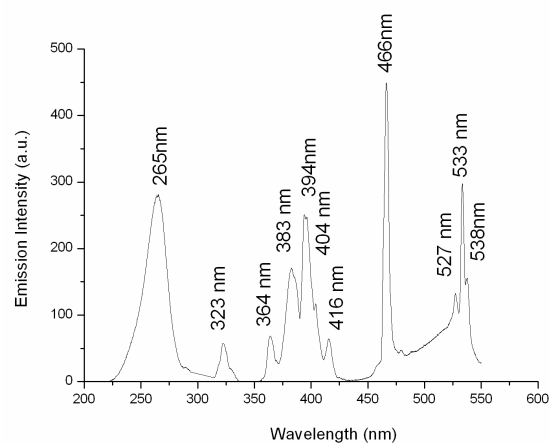
Table 1. Thermal synthesis conditions and some characteristics of some $Y_2O_3:Eu$ (3mol%) phosphors.

Code	Preparative conditions		Phosphor characteristics	
	Temperature ($^{\circ}C$)	Mineralising agent	S_{σ} (m^2/g)	I_{em} (%)
P19	1100	No flux	2.78	73.4
P26a	1100	5% $Na_2B_4O_7$	1.07	51.8
P26b	1100	5% $BaCl_2$	5.03	55.8
P27	1200	No flux	2.20	72.5
P27a	1200	5% $Na_2B_4O_7$	0.63	55.9
P27b	1200	5% $BaCl_2$	2.58	66.9
P27c	1200	5% Na_2CO_3	1.23	80.4
P28	1300	No flux	1.82	82.6
P28a	1300	5% $Na_2B_4O_7$	0.52	50.7
P28b	1300	5% $BaCl_2$	1.70	79.4
P39f	1200	5% $Na_4P_2O_7$	2.90	64.2
P39g	1200	5% Li_2CO_3	0.92	88.6
P39h	1200	5% $Na_4P_2O_7$ + 5% Na_2CO_3	9.40	59.8
P39i	1200	5% $Na_4P_2O_7$ + 5% Li_2CO_3	0.88	98.3
P39j	1200	5% $Na_4P_2O_7$ + 5% Li_2CO_3 + 5% Na_2CO_3	0.75	94.3
P39k	1200	5% $Na_2B_4O_7$ + 5% Li_2CO_3	0.08	88.9
P50g	1200	10% Li_2CO_3	2.20	97.5
P51g	1200	15% Li_2CO_3	1.40	62.0
P52k	1200	5% $Na_2B_4O_7$ + 10% Li_2CO_3	0.26	101.2
P53k	1200	10% $Na_2B_4O_7$ + 5% Li_2CO_3	0.11	87.6

PL properties show that, in our thermal synthesis regime, Y-Eu oxalate-based precursor is converted into yttria cubic crystalline lattice in which, part of the Y^{3+} ions are substituted by Eu^{3+} species. The ionic radii $Eu^{3+} = 0.109$ nm and $Y^{3+} = 0.104$ nm as well as the precursor composition are favorable to the formation of the emission centers.

Fig. 1. Emission spectrum of $Y_2O_3:Eu^{3+}$ ($\lambda_{ex}=254$ nm)

Emission intensity, specific surface area as well as particle size of phosphor powders can be correlated in order to establish the optimum thermal synthesis regime.

Fig. 2. Excitation spectrum of $Y_2O_3:Eu^{3+}$ ($\lambda_{em}=613$ nm)

For no flux samples (P19, P27, P28), emission intensity presents a slight increase with the firing temperature (Fig. 3) simultaneous with the increase of the particle dimensions (Table 1). In the absence of the mineralising agent, the increase of firing temperature does not ensure a good incorporation of the activator into the yttrium oxide matrix, as suggested by the values of the emission intensity (only 82.6% at $1300^{\circ}C$). Therefore the mineralising agent is necessary to improve the PL performances. However, barium chloride, sodium

tetraborate or sodium carbonate does not act as very efficient mineralising agents. Figure 3 reveals that the emission intensity for samples prepared with individual salts, as flux is even smaller than that for samples prepared with no flux. Sodium tetraborate generates the smallest emission intensity (55.9% at 1200°C) that could be explained either by a poor influence on the incorporation of Europium in the matrix, or by a crystalline disorder due to some impurity phases.

It seems that the choice of a proper mineralising agent for the synthesis of a high quality phosphor is a difficult and complex task. The PL improvement can be made by using fluxes in the synthesis mixture (Figure 4). The use of salts mixtures such as lithium carbonate -sodium tetraborate and lithium carbonate -sodium pyrophosphate improves the PL from 73.4% (no flux) to 101.2% and 98.3% respectively. Moreover, the flux amount is also important for both europium incorporation into the yttrium oxide crystalline lattice (formation of luminescent centres) and surface area (particle dimensions) of phosphor powder. The influence of different amounts of lithium carbonate as single flux on the PL and surface area is illustrated in Fig. 5. In this case, optimum PL characteristics and particle dimensions are achieved with 10% wt flux.

The influence of the activator concentration on PL was also investigated based on some $Y_2O_3:Eu^{3+}$ samples prepared with various amounts of europium, namely 3.0 mol % (P27), 5.0 mol % (P29), 7.5 mol % (P30) and 10.0 mol % (P31).

The influence of Europium concentration on PL characteristics is depicted in Fig. 6. The increase of europium amount in the firing mixture is in the favour of formation of luminescent centres and results in the improvement of the emission intensity from 72.5% to 101.6% (for no flux phosphor). The optimal activator concentration is 7.5%; over this value the PL decreases slowly due to the non-radiative processes that take place between Eu-centres (concentration quenching). This discussion is based on the theoretical/calculated value for europium amount. But, in spite of the fact that SimAdd technique permits a good control of the precipitating regime, due to the complexity of the wet-chemical synthesis route, the real concentration of europium in phosphor could be different.

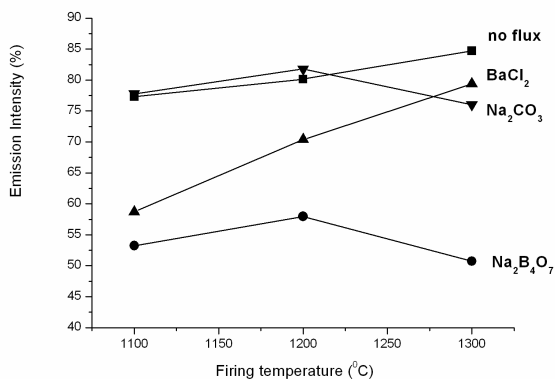


Fig. 3. Influence of the firing temperature on PL intensity for samples prepared with or without flux

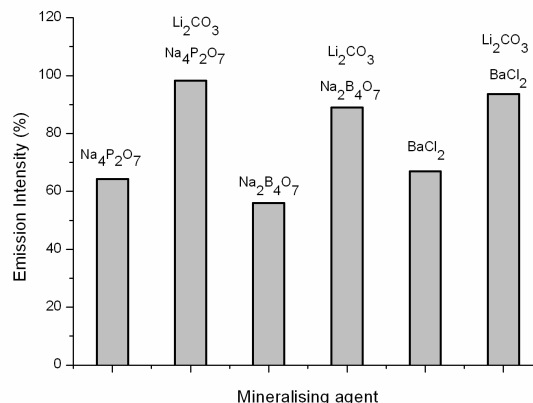


Fig. 4. Influence of the mineralising agent on PL intensity

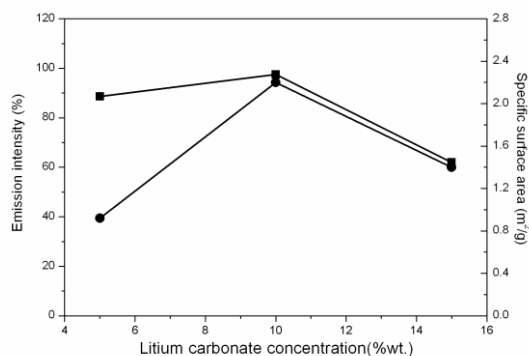


Fig. 5. Influence of the concentration of flux (Li_2CO_3) on PL intensity (square) and specific surface area (circle).

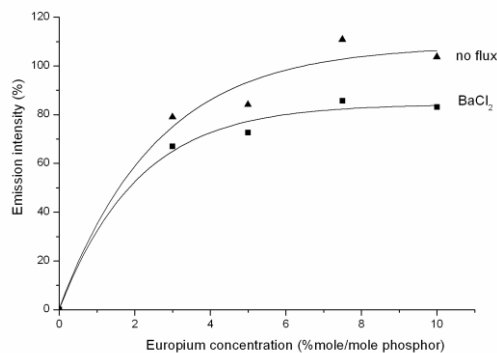


Fig. 6. Influence of europium concentration on emission intensity.

In order to determine the real activator concentration, $Y_2O_3:Eu^{3+}$ samples with variable europium amounts were prepared from precursors obtained in medium with constant acidity (pH = 2), from yttrium-europium nitrate mixtures and oxalic acid. Phosphor synthesis was performed without flux, at 1200°C. Yttrium-europium ratio in phosphors was determined on the basis of

chemical analysis data and compared with the calculated one (Table 2).

Table 2. Yttrium and europium ratio in some $Y_2O_3:Eu^{3+}$ phosphor samples.

Code	Theoretical data		Experimental data		I_{em} (%)
	Y:Eu(wt.)	Phosphor formula	Y:Eu(wt.)	Phosphor formula	
P27	1 :0.0529	$0.970Y_2O_3 \cdot 0.030Eu_2O_3$	1 :0.0685	$0.962Y_2O_3 \cdot 0.038Eu_2O_3$	72.5
P29	1 :0.0901	$0.950Y_2O_3 \cdot 0.050Eu_2O_3$	1 :0.1087	$0.940Y_2O_3 \cdot 0.060Eu_2O_3$	77.2
P30	1 :0.1389	$0.925Y_2O_3 \cdot 0.075Eu_2O_3$	1 :0.1563	$0.916Y_2O_3 \cdot 0.084Eu_2O_3$	101.6
P31	1 :0.1923	$0.900Y_2O_3 \cdot 0.100Eu_2O_3$	1 :0.2381	$0.878Y_2O_3 \cdot 0.122Eu_2O_3$	95.1

One can be seen that, in phosphor samples, the real Europium concentration is with about 20 ÷ 30% higher than the calculated value, thus illustrating that the precipitation of europium and yttrium is achieved with variable rates. The fact that the difference between the theoretical and experimental values does not show a monotonous evolution trend illustrates the complexity of the precipitation process. The formation of precursor is influenced by both the solubility of europium and yttrium basic oxalates and the local precipitation parameters.

Crystalline structure of phosphors is also influence by the mineralizing agent. Fig. 7 presents the XRD patterns for two phosphor samples, namely P27 (no flux) and P27a (sodium tetraborate) in comparison with the precursor.

XRD patterns illustrate that precursor and $Y_2O_3:Eu^{3+}$ phosphors consist of well-formed crystalline phases. $Y_2O_3:Eu^{3+}$ powders are relatively homogeneous and well crystallized powders with cubic structure, which illustrate the formation of $Y_2O_3-Eu_2O_3$ solid solutions in agreement with the literature data ($Y_{1.90}Eu_{0.10}O_3$; PDF251105). One can note that, in comparison with the no flux phosphor, the luminescent material obtained with sodium tetraborate shows additional XRD lines situated at $2\theta = 31.10, 31.64, 32.34, 32.79, 35.52$ and 38.20° . These ones can be assigned to monoclinic yttrium borate (Y_3BO_6 ; PDF340261), a side product that accompanies the cubic $Y_2O_3:Eu^{3+}$ formation during the firing stage. This structural inhomogeneity is probable responsible for the relative low emission intensity of samples P26a, P27a and P28a.

The effective crystallite size D_{eff} and the root mean square of the microstrains averaged along [222], [400], [440] and [622] directions ($\langle \varepsilon^2 \rangle^{1/2}$) of phosphor powders, determined on the basis of band profile analysis, depend on the thermal synthesis regime. The flux effect is put in evidence by the variation of the microstructural parameters. For instance, D_{eff} increases in order: P27 (no flux) – 38.5nm; P27a ($Na_2B_4O_7$) – 40.5 nm, P27b ($BaCl_2$) – 130.8 nm. In comparison with P27, P27a and P27b, sample P27c (Na_2CO_3) presents a different distribution curve of the crystallite dimensions; there are two distribution maxima situated at 26.6 nm and 52.7 nm. This behavior indicates an inhomogeneous sample at crystallite level. As for the crystallite lattice microstrains, the $\langle \varepsilon^2 \rangle^{1/2}$ values are situated between $0.438 \cdot 10^{-3}$ and $0.242 \cdot 10^{-2}$. Depending on the mineralising agent, the cell unit

parameter of the crystalline lattice of phosphors prepared with different fluxes are variable and a little smaller than the theoretical value ($a=1.0604$ nm) as follows: 1.0588nm for P27a ($Na_2B_4O_7$), 1.0555 nm for P27b ($BaCl_2$) and 1.0579 nm for P27c (Na_2CO_3).

The mineralizing agent and temperature could also influence the phosphor *particle morphology and size*, as illustrated by the SEM images (fig.8).

Platelets-like particles of precursor of about 1.5 μm are converted into conglomerates with irregular shapes, formed from more or less dispersed primary particles. The thermal treatment performed without flux leads to 1.0 ÷ 3.0 μm agglomerates of spherical primary particles of about 0.5 μm (P27). Phosphor powders prepared with mineralising agent are aggregates of spherical or elongated particles with variable dimensions. Depending on the flux, the size of primary particles increase or decrease in comparison with the no-flux phosphor, as follows: $\sim 1.0 \div 3.5 \mu m$ for P27a ($Na_2B_4O_7$), $\sim 0.1-0.3 \mu m$ for P27b ($BaCl_2$) and $\sim 1.2 - 1.5 \mu m$ for P27c (Na_2CO_3).

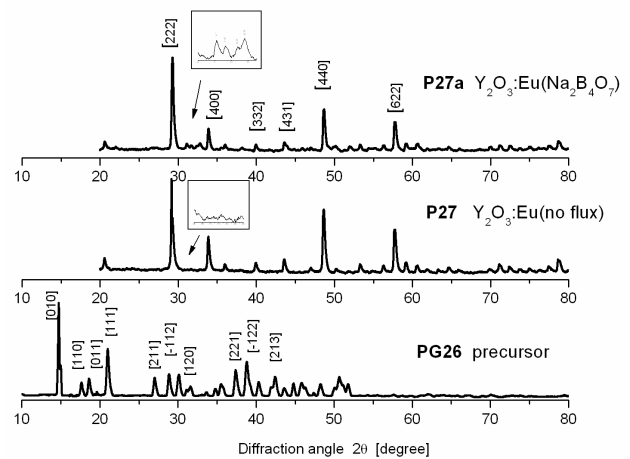


Fig. 7. XRD patterns for precursor and $Y_2O_3:Eu^{3+}$ samples P27 and P27a (CuKa radiation).

Large conglomerates of particles could be prepared when lithium and/or sodium and/or barium salts mixtures were used as mineralising agents. Depending on the flux and firing temperature, phosphors with variable particle dimensions, from $\sim 0.1 \mu m$ to $\sim 100 \mu m$ could be obtained

from the Y-Eu oxalate-based precursors prepared by *SimAdd* precipitation technique.

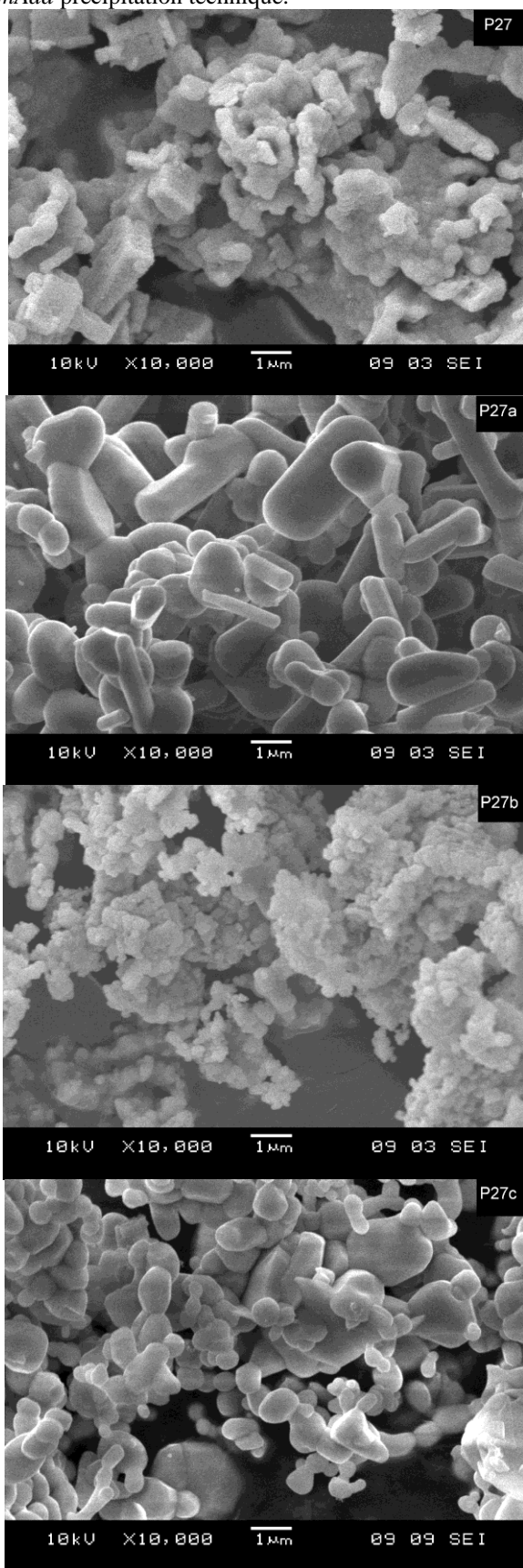


Fig. 8. SEM images for some yttrium oxide phosphors prepared with different mineralising agents: no flux (P27), $\text{Na}_2\text{B}_4\text{O}_7$ (P27a), BaCl_2 (P27b), Na_2CO_3 (P27c)

4. Conclusions

Various $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ samples were prepared by thermal treatment of Yttrium/Europium precursor in well-controlled conditions. The preparation of yttrium oxalate-based precursor was performed by wet chemical method, by simultaneous addition technique.

It was put in evidence that different thermal synthesis conditions generate $\text{Y}_2\text{O}_3:\text{Eu}^{3+}$ phosphors with variable particle size and morphology and PL characteristics. Depending on the mineralising agent and temperature used during the thermal synthesis stage, phosphors with variable particle dimensions, from $\sim 0.1\mu\text{m}$ to $\sim 100\mu\text{m}$ could be prepared. The increase of the firing temperature generates an enhancement of the emission intensity of the phosphor samples. The mineralising agent and the firing temperature determine the incorporation degree of Eu-activator into the yttria crystalline lattice and consequently the PL performances. The best results were obtained with lithium carbonate alone or in mixture with sodium tetraborate or sodium pyrophosphate in flux.

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