

Dedicated to professor Gh. Marcu at his 80th anniversary

SPECTRAL INVESTIGATIONS OF EUROPIUM ACTIVATED YTTRIUM OXIDE PHOSPHOR PREPARED BY COPRECIPITATION METHOD WITH OXALIC ACID

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ABSTRACT. Europium activated yttrium oxide phosphors were prepared by reagent simultaneous addition technique, using oxalic acid as precipitating reagent. The aim of the paper was to study the influence of the firing conditions on luminescent and morpho-structural properties of $Y_2O_3:Eu$ phosphors. Thermal analysis, X-ray diffraction, SEM, FTIR and fluorescence spectroscopy were used to investigate precursor and phosphor powders. The correlation between the phosphor properties and precursor quality enabled us to select the optimal synthesis conditions.

Keywords: yttrium oxide, phosphors, luminescence; wet chemical method

INTRODUCTION

Europium activated yttrium oxide ($Y_2O_3:Eu$) is a well-known red emitting phosphor used for applications in displays, optoelectronic devices and fluorescent lamps [1-3]. Phosphor utilisations depend on luminescence performances and powder characteristics that are defined during the synthesis stages. Luminescence characteristics, particle morphology and size or crystalline order degree are factors that determine the use of phosphor powders in optoelectronic devices.

Conventionally, $Y_2O_3:Eu$ powders are prepared from yttrium/europium oxide mixture, by the ceramic method that implies high firing temperature and long thermal treatment periods [4]. Mild thermal synthesis conditions could be used when oxides species are generated from precursors obtained through the wet-chemical preparation route.

The paper presents several results referring to the synthesis of fine powders of $Y_2O_3:Eu$ phosphor from yttrium/europium oxalate precursor obtained by the wet chemical route. The co-precipitated precursor was prepared by using the reagent simultaneously addition technique –*SimAdd* developed in our previous works [5-7].

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In this purpose, europium containing yttrium oxalate based precursor was obtained under well controlled precipitation conditions from yttrium-europium nitrate and oxalic acid solutions and was converted into phosphors in different thermal treatment conditions. Spectral investigations as well as scanning electron microscopy (SEM) and thermal analysis were used for precursor and phosphors characterisation. A correlation between the preparation conditions and precursor and phosphors characteristics was established in order to improve the *SimAdd* technique for the obtaining of fine powders of europium activated yttrium oxide phosphors.

EXPERIMENTAL PART

Europium activated yttrium oxide phosphors (Y_2O_3 : Eu (3 mol%)) were prepared from yttrium-europium oxalate precursor.

Yttrium-europium precursor (sample code PG26) was prepared by the wet chemical method, using the simultaneous addition (*SimAdd*) technique of reagents into a bottom solution. Equal volumes of oxalic acid (0.45M) as precipitating reagent and yttrium-europium nitrate solution (0.30M) were simultaneously added, with equal constant flow ($\sim 5.7 \text{ mL min}^{-1}$), into a diluted solution of oxalic acid. Precipitation was carried out at 80°C , under continuous stirring and pH monitoring. During the precipitation stage, the pH of the bottom solution was adjusted with ammonia to 2. The precursor post-precipitation treatment consisted of 24 h aging (maturation stage), water wash and drying. Yttrium-europium oxalate precursor was fired for 2 hrs in air, at 1100°C , 1200°C and 1300°C to provide the corresponding phosphor powder, P19, P27 and P28, respectively. No flux was used for the phosphor thermal synthesis stage. The as obtained materials were water washed, dried and sieved.

Precursors and phosphors were characterised by thermal analysis-TG-DTG-DTA curves (Paulik –Erdely Derivatograf OD-102; heating rate 6°C/min), infrared absorption spectroscopy -FTIR spectra (JASKO 610 FTIR Spectrometer; KBr pellets technique), photoluminescence measurements –PL spectra (JASKO FP-6500 Spectrofluorimeter Wavel; $\lambda_{\text{exc}}=254\text{nm}$), X-ray diffraction–XRD patterns (D8Advanced Brucker Diffractometer, $\text{CuK}\alpha$ radiation) and Scanning Electronic Microscopy-SEM images (JEOL –JSM 5510LV Microscope; Au-coated powders) .

RESULTS AND DISCUSSION

This main aim of the study was to clarify some aspects concerning the synthesis of very fine particles of Y_2O_3 : Eu phosphors by wet chemical method, using the reagent simultaneous addition technique -*SimAdd*. The precursor was prepared by co-precipitation, from yttrium-europium nitrate mixture and oxalic acid.

Mention has to be made that in precursor and phosphor samples, about 3 mole% of yttrium was replaced by europium. It is supposed that, excepting the PL properties, the isovalent substitution of Y^{3+} with small amounts of Eu^{3+} does not influence the general characteristics of precursor and phosphors so that its presence is neglected during the discussion.

For the beginning, the precursor composition was estimated on the basis of the thermal analysis. TG-DTG-DTA curves of the PG26 precursor show that the thermal decomposition proceeds in three major steps. These steps can be associated

with water loss ($\sim 191^{\circ}\text{C}$), decomposition of the metallic oxalate ($\sim 408^{\circ}\text{C}$) and probable, decomposition of the metallic oxy-carbonate intermediate ($\sim 530^{\circ}\text{C}$).

Assuming that the precursor is a metallic basic oxalate and taking into consideration the literature data [8], the yttrium oxide phosphor formation could be described by the following conversion path:



It is well known that the thermal synthesis conditions determine the phosphor characteristics [9]. In the present study, three phosphor samples were prepared in different thermal regime, namely P19 (1100°C), P27 (1200°C) and P28 (1300°C).

In order to correlate the precursor characteristics with the properties of the corresponding Y_2O_3 : Eu phosphors, FTIR spectra and XRD spectra were registered and comparatively analysed. **Fig. 1** and **2** presents FTIR and XRD spectra for PG26 and P27 samples.

The precursor vibrational spectrum consists of some characteristic bands i.e. ν (H-O) ~ 3470 , ν (C=O) ~ 1634 , ν (C-O) ~ 1324 , δ (O-C=O)+(Y-OH) ~ 814 -790. After the thermal treatment, the precursor specific FTIR bands disappear and the characteristic vibration of Y-O bond, at $\sim 560\text{cm}^{-1}$ can be observed. FTIR spectra suggest the complete conversion of yttrium oxalate-based precursor into yttrium oxide phosphors.

XRD spectra illustrate that all Y_2O_3 : Eu phosphor samples as well as the parent precursor consist of well-formed crystalline phases. According to the literature, the yttrium oxalate-based precursor contains mostly the crystalline phase of yttrium ammonium oxalate (PDF 221047). All Y_2O_3 : Eu powders are homogeneous and well crystallized, which demonstrate the formation of Y_2O_3 - Eu_2O_3 solid solutions with cubic structure (PDF411105).

The XRD measurements suggest that yttrium-based precursor contains NH_4^+ ions. One can suppose that the specific ammonium infrared vibrations, i.e. ν (N-H) and δ (N-H), are covered by those of the basic yttrium oxalate.

According to the XRD and FTIR spectra, the precursor can be formulated as: $[\text{Y}_{2-2x}(\text{NH}_4)_{2x}][(\text{C}_2\text{O}_4)_{3-3y}(\text{OH})_{3y}] \cdot z\text{H}_2\text{O}$ where $0 < x < 1$; $0 < y < 1$.

The thermal treatment of yttrium-oxalate based precursors at 1100 - 1300°C ensures the incorporation of Eu^{3+} ions into the Y_2O_3 cubic crystalline lattice and the formation of luminescent centres.

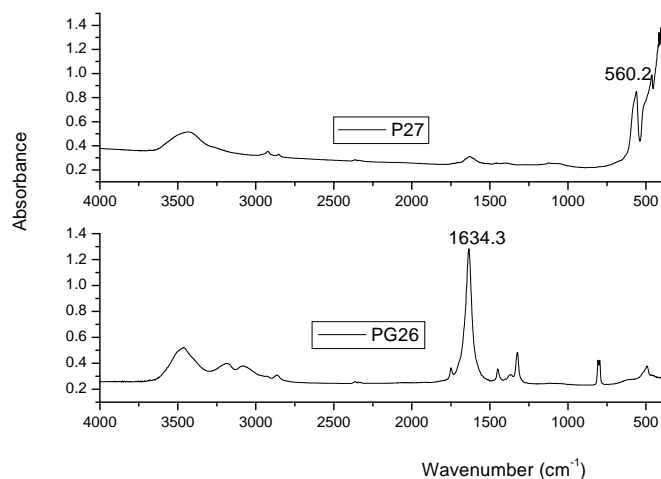


FIG. 1. FT-IR SPECTRA FOR PRECURSOR (PG26) and phosphor (P27) prepared at 1200 °C

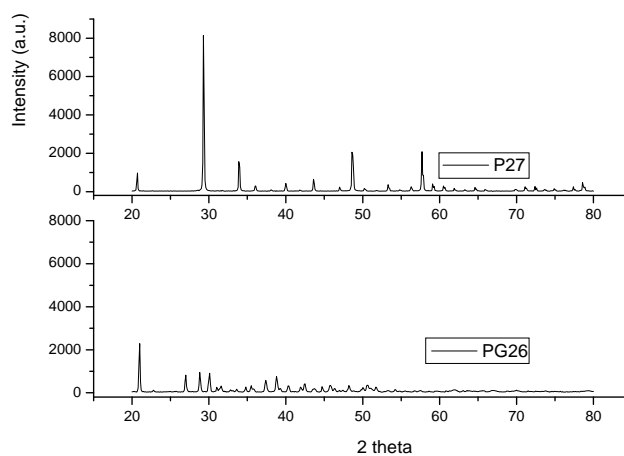


Fig. 2. XRD patterns for precursor (PG26) and phosphor (P27) prepared at 1200 °C

Fig. 3 presents the emission spectra of yttrium oxide phosphor (P19) registered for different excitation radiations.

On the basis of phosphor emission spectra, the PL intensity of the main emission peak was evaluated in comparison with the standard (Kemira, $I_{611\text{nm}}=100\%$). Under 254 nm excitation, the phosphor emits mainly in the red domain, i.e. at ~ 590 nm ($^5D_0 \rightarrow ^7F_1$ electronic transition) and ~611 nm ($^5D_0 \rightarrow ^7F_2$

transition). The excitation radiation influences the emission intensity and even the ratio between the different emission bands.

The phosphor thermal synthesis regime determines the red emission intensity of $\text{Y}_2\text{O}_3:\text{Eu}$ phosphors (**Fig. 4**). The emission intensity slightly increases with the firing temperature from 74.3% (P19) to 80.2% (P27) and 84.7% (P28) for 254 nm excitation and from 31.4% (P19) to 47.5% (P27) and 48.0% (P28) under 365 nm radiation excitation.

Phosphor morphology and particle size depend on the precursor characteristics and the thermal synthesis regime. The SEM images of phosphor P27 prepared at 1200°C and of the corresponding precursor PG26 are presented in **Fig. 5**.

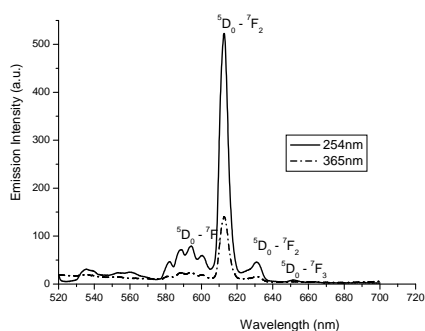


Fig. 3. Emission spectra of P19 phosphor samples

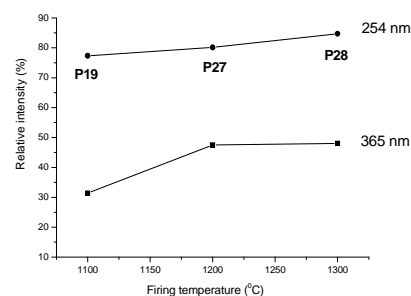


Fig. 4. Influence of synthesis temperature on the PL emission intensity

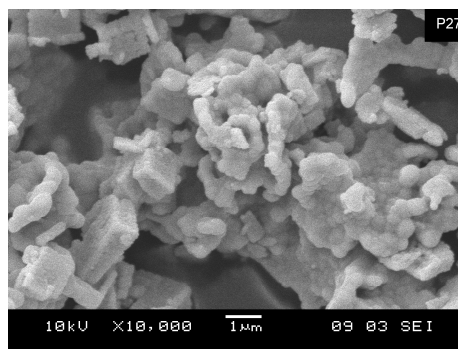
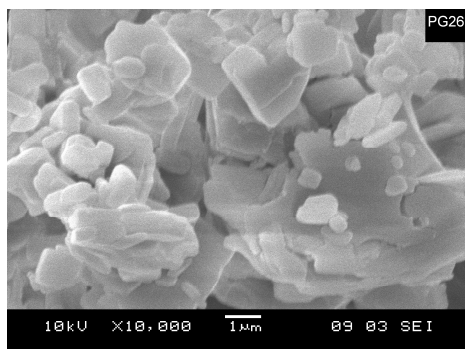


Fig. 5. SEM images of precursor (left) and phosphor (right)

Platelets like particle of precursor are converted into conglomerates, with irregular shape, of small particles. As illustrated by the SEM images, the thermal treatment performed without flux leads to a partial conversion of precursor platelets of $1 \div 3 \mu\text{m}$ to more or less dispersed spherical primary phosphor particles of $\sim 0.5 \mu\text{m}$.

The thermal treatment induces a decrease of the particle size due to the decomposition. The incomplete morphological conversion suggests that, during the

phosphor thermal synthesis, some mineralising agents (fluxes) need to be added to the yttrium-based precursor.

CONCLUSIONS

The *wet chemical synthesis method*, especially the *SimAdd* technique, facilitates the control of some preparative parameters for obtaining the yttrium oxalate based-precursor for $Y_2O_3:Eu$ powders with small particle sizes. XRD and FTIR spectral investigations suggest that the precursor is mainly a hydrated yttrium-ammonium oxalate. Additional PL and SEM measurements revealed that the firing temperature influences the luminescence characteristics and the morpho-structural properties of phosphors particles obtained by the *SimAdd* technique, from precursor prepared with oxalic acid as precipitating reagent. Further experiments are to be performed in order to improve the PL characteristics and powder morphological characteristics.

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REFERENCES

1. R.P. Rao, *Solid State Comm.*, **1996**, 99, 439-443.
2. M.H. Lee, S.G. Oh, S.C.Yi, D.S.Seo, J.P.Hong, C.O.Kim, Y.K.Yoo, J.S.Yoo, *J. Electrochem. Soc.*, **2000**, 147, 3139-3142.
3. X. Jing, T. Ireland, G.Gibbons, D.J.Barber, J.Silver, A.Vecht, G.Fern, P.Trowga, D.G.Morton, *J. Electrochem.Soc.*, **1999**, 146, 4654-4658.
4. M.N. Nazarov, J.H. Khang, D.Y. Jeon, E.J. Popovici, L.Muresan, B.S.Tsukerblat, *Solid State Comm.*, **2005**, 133, 183-186.
5. A. Hristea, E.J. Popovici, L.Muresan, R.Grecu, E.Indrea, M.Voicescu, *Studia Universitatis Babes Bolyai, Seria Physica*, XLIX, **2004**, 185-188.
6. L. Muresan, E. J. Popovici, A.Hristea, M.Vasilescu, I.Silaghi-Dumitrescu, *Studia Universitatis Babes Bolyai, Seria Physica*, XLIX, **2004**,182-184.
7. E-J. Popovici, L. Muresan, H.Amalia, E. Indrea, M. Vasilescu, *J. Alloys. Comp.* (in press)
8. M.J.Fuller, J.Pinkstone, *J.Less.Common.Metals*, **1980**, 70, 127-134.
9. G.Blasse, B.C.Grabmaier, „Luminescent materials”, Springer Ver.,Berlin, **1994**.