ELSEVIER

Journal of Alloys and Compounds 303–304 (2000) 316–319

Journal of ALLOYS AND COMPOUNDS

www.elsevier.com/locate/jallcom

A new procedure to obtain Eu^{3+} doped oxide and oxosalt phosphors

Osvaldo A. Serra*, Simone A. Cicillini, Renata R. Ishiki

Laboratory of Rare Earths, Chemistry Department, FFCLRP, University of São Paulo, Av. Bandeirantes 3900, CEP 14040-901 Ribeirão Preto, SP, Brazil

---

Abstract

A different route to the synthesis of Eu^{3+} phosphors in matrices such as Y_2O_3, YVO_4, $La(BO_3)_3$ or $YNbO_4$, and the characterization and luminescent properties of these compounds, were studied. The new route (Pechini method) consists of the formation of a polymeric resin obtained by polyesterification between metal chelate complexes (formed by metallic ions and α-hydroxycarboxylic acids) and a polyfunctional alcohol. Ignition of this resin at low temperature renders the selected composition of Eu^{3+} doped oxides or oxosalts. Luminescent and X-ray spectroscopy and thermogravimetric analysis were used to characterize the materials.

Keywords: Europium; Luminescence; Polymer; Phosphor; Pechini

---

1. Introduction

Luminescent materials, also called phosphors, can be found in a broad range of every-day applications such as cathode ray tubes (CRTs), projection televisions (PVTs), fluorescent tubes and X-ray detectors. The clever tricolor concept, introduced in fluorescent lamps almost 30 years ago, together with the unique properties of rare-earth metal ions has revolutionized the lighting market [1]. These uses are essentially based on diluted phosphors in appropriate networks. A wide range of emissions can be obtained, depending on the nature of the employed activator and the respective positions of the excited and fundamental energy states. Nowadays, the three basic emission colors blue, green and red can be obtained only with rare-earth materials. The reconstitution of daylight is possible with the primary emissions at 450, 550 and 610 nm of appropriate Eu^{2+}, Tb^{3+} and Eu^{3+} doped compounds [2]. The luminescent properties of lanthanide ions, such as lifetimes and width of absorption and emission bands, are due to the electronic transitions in the protected $4f^n$ configuration [3,4]. Since the fifties, materials have been synthesized by several different methodologies [5–10]. In the search for new luminescent materials and also for different routes to obtain Eu^{3+} phosphors in matrices such as Y_2O_3, YVO_4, $La(BO_3)_3$ or $YNbO_4$, we introduced the use of the Pechini [11] method. This method is primarily used to obtain oxide electrodes and begins with polybasic chelates that are formed between hydroxycarboxylic acids (e.g., citric acid) and metallic ions. The chelate undergoes polyesterification upon heating with a polyfunctional alcohol (e.g., ethylene glycol) to form a resin intermediate. Ignition of this resin at low temperature removes the organic material and renders the selected composition of Eu^{3+} doped oxides or oxosalts. Among the advantages of this method are the possibility to prepare complex compositions, good homogeneity through mixing at the molecular level in solution and stoichiometry control [12]. Therefore, a temperature of only ~600°C is necessary for the synthesis of the materials, in contrast to the 900°C or even higher temperatures used in the case of oxides and oxosalts.

2. Experimental procedure

First we prepared rare-earth citrates by direct reaction of the appropriate mixture of the Eu^{3+} (activator) and Y^{3+} or La^{3+} precursors (Eu_2O_3, Y_2O_3 and La_2O_3) with citric acid in aqueous media, under heating. After dissolution of the oxides we added a soluble precursor, $(NH_3)_3VO_4$, H_3BO_3, or $NH_4H_2[NbO(C_2O_4)_3]\cdot 3H_2O$. To obtain the polymeric resin (polyester) we added ethylene glycol and heated the mixture at 130°C. The yellowish resin was fired at ~600°C in air leading to the luminescent powders.

The excitation and emission spectra were recorded at room temperature with a SPEX-Fluorolog II. Luminescent decay curves were measured under pulsed Xe lamp excitation using a phosphorimeter (SPEX 1934D). The

---

*Corresponding author.

0925-8388/00/$ – see front matter © 2000 Elsevier Science S.A. All rights reserved.
PII: S0925-8388(00)00595-8

crystallinity of the compounds was observed by X-ray powder diffraction (XRD) (D 5005 X-Ray Diffractometer, Siemens). For the Y_2O_3:Eu^{3+} sample, we followed resin decomposition by TGA/DTA carried out in air, with a heating rate of 20°C/min, from 25 to 680°C (Thermal Analyst 2100, TA Instruments SDT 2960 — Simultaneous DTA-TGA).

3. Results and discussion

Excitation spectra for Eu^{3+} phosphors in Y_2O_3, $La(BO_3)_3$ and $YNbO_4$ (Fig. 1) present a maximum at ~393 nm, which we ascribed to the $^5L_6$ level of Eu^{3+} [13–15]. In the excitation spectrum of YVO_4:Eu^{3+} the maximum was observed at 314 nm due to the vanadate matrix. In YVO_4 the Stokes shift is ~10,000 cm^{-1}. This makes YVO_4:Eu^{3+} a very efficient red phosphor: excitation into the vanadate group (31,850 cm^{-1}) is followed by energy migration over the vanadate groups to Eu^{3+} centers. The blue emission of the pure YVO_4 is very weak at room temperature [7].

The emission spectra (Figs. 2 and 3) of the compounds obtained present characteristic Eu^{3+} emission transitions arising mainly from the $^5D_0$ level to the ^7F_J ($J = 0, 1, 2, 3, 4$) manifolds [13–15].

For YVO_4:Eu^{3+}, $La(BO_3)_3$:Eu^{3+} and $YNbO_4$:Eu^{3+}, the emission spectra also show the emission transition $^5D_1 \rightarrow {}^7F_J$ ($J = 1, 2$) levels [13].

In these emission spectra, the band corresponding to the $^5D_0 \rightarrow {}^7F_2$ transition has a larger amplitude than that due to $^5D_0 \rightarrow {}^7F_1$, which is an indication that the symmetry around Eu^{3+} does not contain a center of inversion [16–18]. The presence of the $^5D_0 \rightarrow {}^7F_0$ transition indicates that Eu^{3+} is located in one of the C_{nv}, C_n or C_s symmetry groups [17]. The relative intensities of the $^5D_0 \rightarrow {}^7F_2$ and also the integrated area of the $^5D_0 \rightarrow {}^7F_{0,1,2}$ transitions are

$$YVO_4{:}Eu^{3+} > La(BO_3)_3{:}Eu^{3+} > YNbO_4{:}Eu^{3+} > Y_2O_3{:}Eu^{3+}$$

The decay curve for the $^5D_0$ level ($^5D_0 \rightarrow {}^7F_2$ transition) could be well fitted with a single exponential function and, in agreement with the observation of a single $^5D_0 \rightarrow {}^7F_0$ transition, indicates that there is only one Eu^{3+} site in the oxides or oxosalts. The decay time for Y_2O_3:Eu^{3+} is in agreement with the value published by Blasse [7]. Table 1 shows the lifetimes for the $^5D_0$ level of Eu^{3+} in the compounds; these values are in agreement with the relative intensity sequence already mentioned.

The doped Y_2O_3 (~5% in Eu^{3+}) produced by us has approximately the same photophysical properties as the Rhône-Poulenc Y_2O_3:Eu^{3+} standard. The TGA/DTA data (Fig. 4) used to follow the Y_2O_3:Eu^{3+} preparation showed exothermic peaks at ~400 and 520°C. The peak at about 400°C appeared to be due to the decomposition of organic material. The peak at about 520°C corresponded to the crystallization of doped yttrium oxide [19].

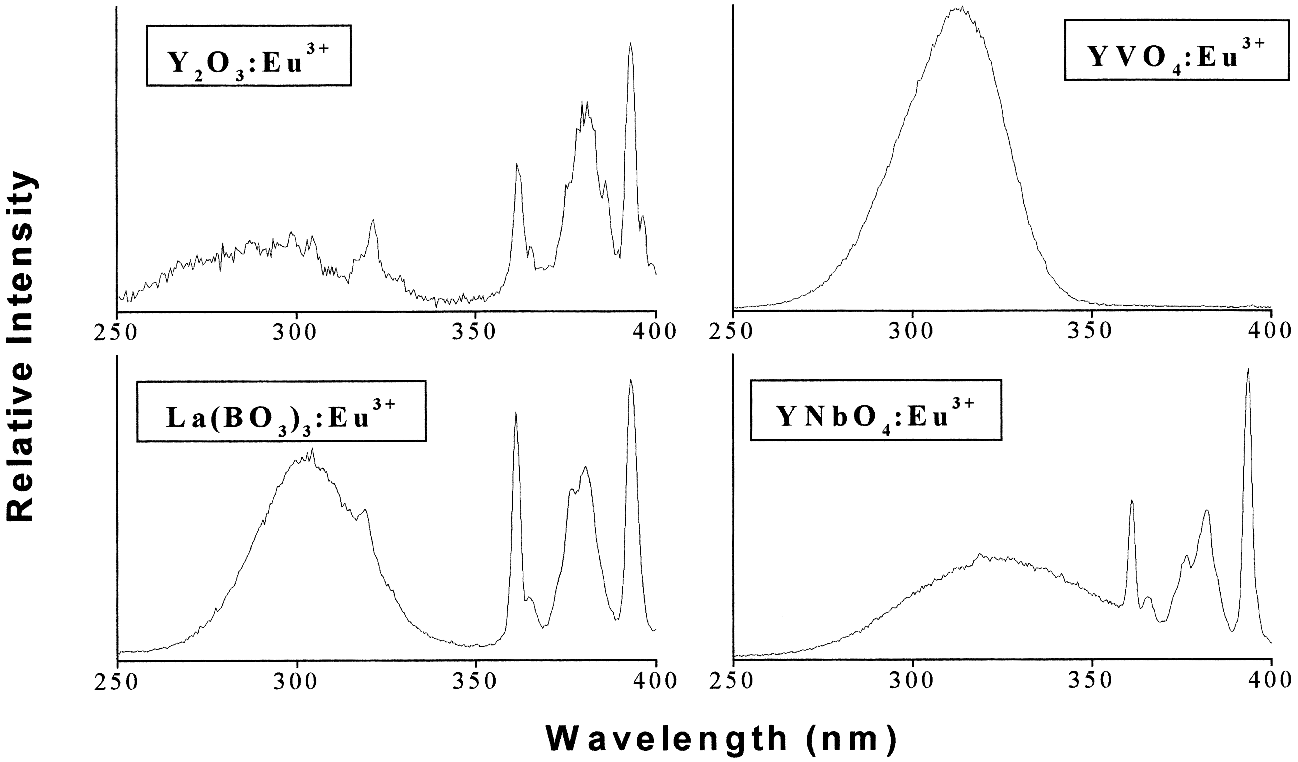

Fig. 1. Excitation spectra of Y_2O_3:Eu^{3+}, YVO_4:Eu^{3+}, $La(BO_3)_3$:Eu^{3+} and $YNbO_4$:Eu^{3+} ($\lambda_{em} = 614$ nm) at 25°C.

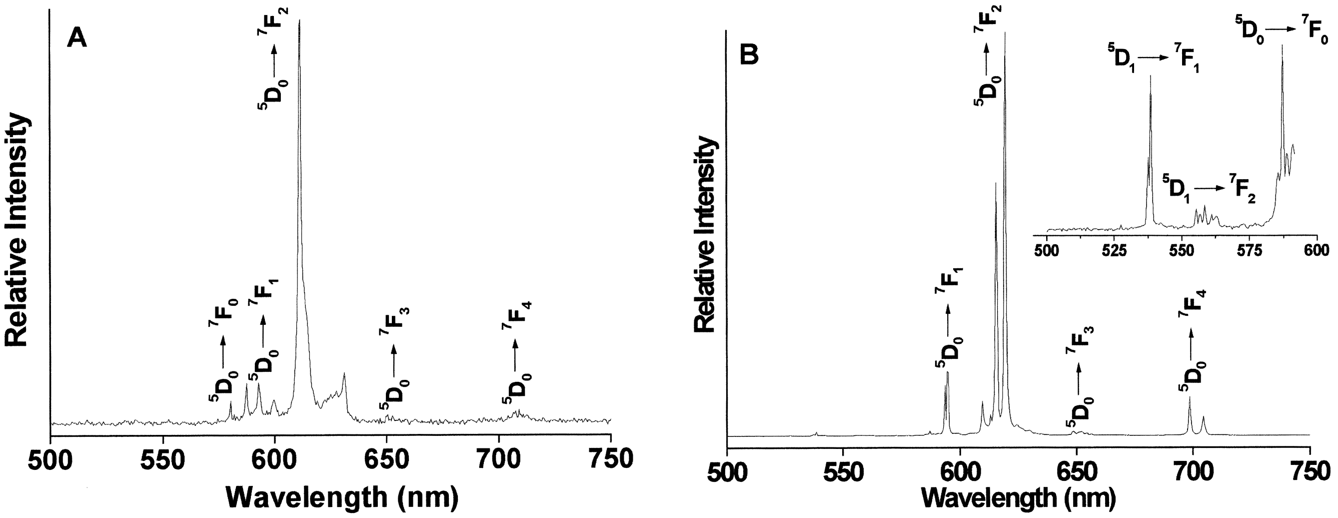

Fig. 2. Emission spectra of (A) Y_2O_3:Eu^{3+} (λ_{ex} = 393 nm) and (B) YVO_4:Eu^{3+} (λ_{ex} = 314 nm) at 25°C.

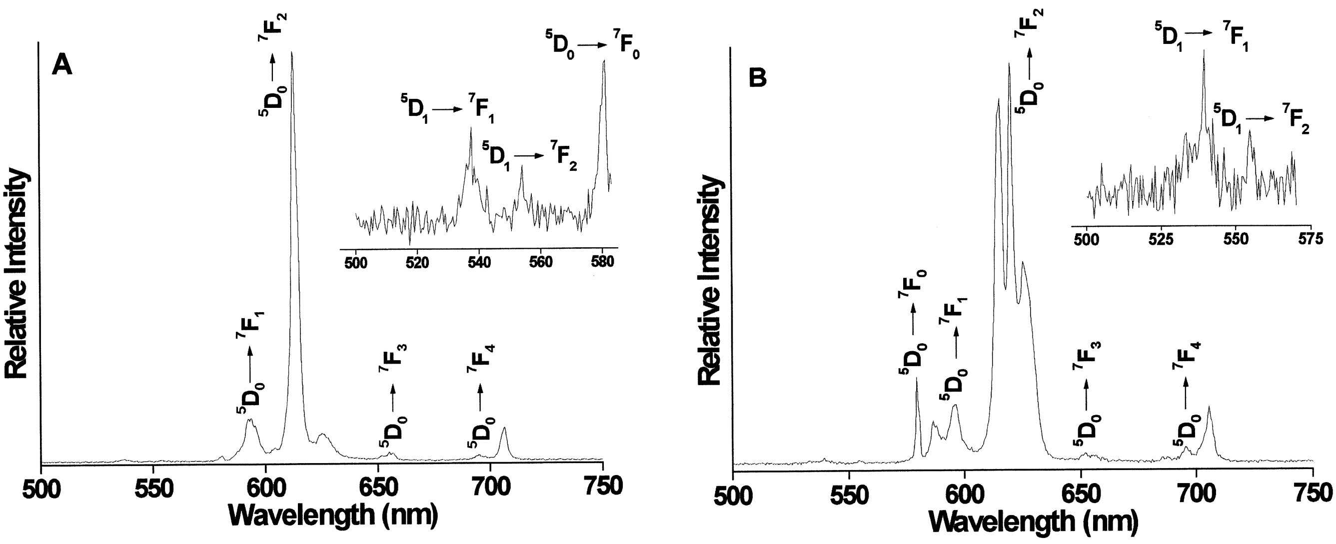

Fig. 3. Emission spectra of (A) $YNbO_4$:Eu^{3+} and (B) $La(BO_3)_3$:Eu^{3+} (λ_{ex} = 393 nm) at 25°C.

The X-ray powder diffraction patterns (Fig. 5) of Y_2O_3:Eu^{3+} and YVO_4:Eu^{3+} samples presented characteristics lines of standard compounds [20]. $YNbO_4$:Eu^{3+} and $La(BO_3)_3$:Eu^{3+} are not very crystalline.

4. Conclusion

Y_2O_3:Eu^{3+}, YVO_4:Eu^{3+}, $YNbO_4$:Eu^{3+} and $La(BO_3)_3$:Eu^{3+} red phosphor powders can be prepared by

Table 1
Lifetimes (τ) ($^5D_0$ level) of the synthesized oxides and oxosalts

	Sample			
	Y_2O_3:Eu^{3+} λ_{ex} = 393 nm	YVO_4:Eu^{3+} λ_{ex} = 314 nm	$YNbO_4$:Eu^{3+} λ_{ex} = 393.5 nm	$La(BO_3)_3$:Eu^{3+} λ_{ex} = 393 nm
τ (ms)	1.03	1.35	1.15	1.30

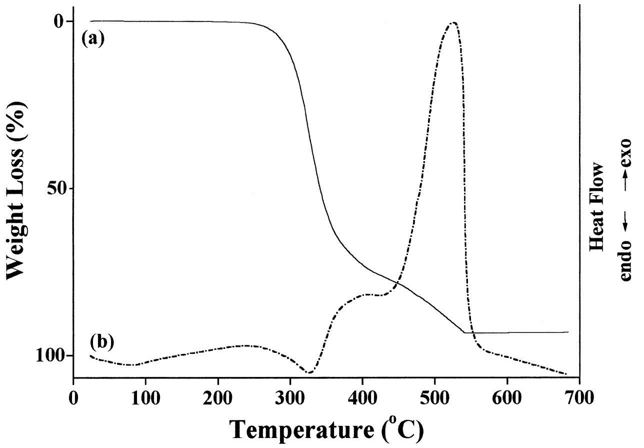

Fig. 4. (a) TGA and (b) DTA curve for Y_2O_3:Eu^{3+} resin decomposition; a 15.35 mg sample heated from 25 to 680°C in air at a heating rate of 20°C/min.

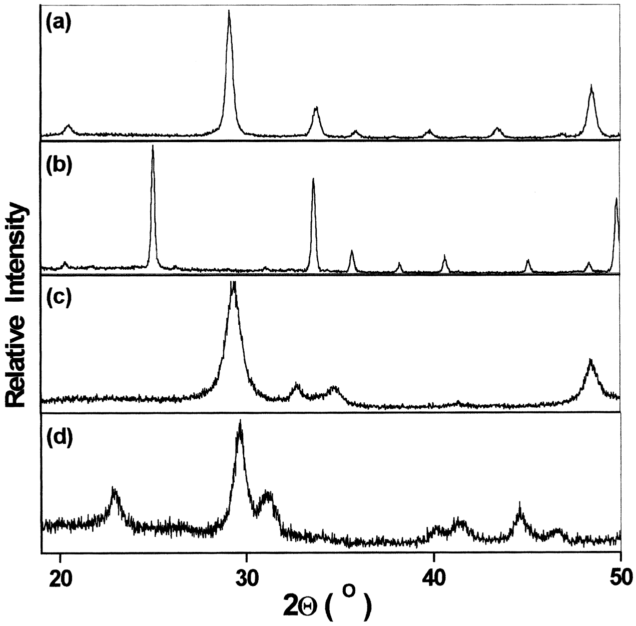

Fig. 5. X-ray powder diffraction patterns of (a) Y_2O_3:Eu^{3+}, (b) YVO_4:Eu^{3+}, (c) $YNbO_4$:Eu^{3+} and (d) $La(BO_3)_3$:Eu^{3+}.

the Pechini method using lower firing temperatures than conventional methods without loss of photophysical properties. The YVO_4:Eu^{3+} produced presented higher luminescence than the other compounds.

Acknowledgements

We thank the Brazilian agencies FAPESP, CNPq and CAPES for financial support.

References

[1] T. Jüstel, H. Nikol, C. Ronda, Angew. Chem. Int. Ed. 37 (1998) 3084.
[2] P. Maestro, in: Material Today and Tomorrow, Rhône-Poulenc, Paris, 1991, p. 301.
[3] O.A. Serra, I.L.V. Rosa, C.L. Medeiros, M.E.D. Zaniquelli, J. Lumin. 60/61 (1994) 112.
[4] O.A. Serra, E.J. Nassar, C.A. Kodaira, C.R. Neri, P.S. Calefi, I.L.V. Rosa, Spectrochim. Acta A 54 (1998) 2077.
[5] E. Baudrin, S. Denis, F. Orsini, L. Seguin, M. Touboul, J.M. Tarascon, J. Mater. Chem. 9 (1) (1999) 101.
[6] J. Livage, Coord. Chem. Rev. 180 (1998) 999.
[7] G. Blasse, B.C. Grabmaier, Luminescent Materials, Springer, Berlin, 1994.
[8] O.A. Serra, E.J. Nassar, G. Zapparolli, I.L.V. Rosa, J. Alloys Comp. 225 (1995) 63.
[9] O.A. Serra, E.J. Nassar, I.L.V. Rosa, J. Lumin. 72–74 (1997) 263.
[10] S.A. Cicillini, P.S. Calefi, C.R. Neri, E.J. Nassar, O.A. Serra, J. Non-Cryst. Solids 247 (1999) 114.
[11] M.P. Pechini, US Patent 3 330 697 (1967).
[12] D. Segal, J. Mater. Chem. 7 (1997) 1297.
[13] O.A. Serra, L.C. Thompson, Inorg. Chem. 15 (1976) 504.
[14] J.-C.G. Bünzli, in: J.-C.G. Bünzli, G.R. Choppin (Eds.), Lanthanide Probes in Life, Chemical and Earth Sciences, Elsevier, New York, 1989, Chapter 7.
[15] S.J.L. Ribeiro, K. Dahmouche, C.A. Ribeiro, C.V. Santilli, S.H. Pulcinelli, J. Sol-Gel Sci. Techn. 13 (1998) 427.
[16] C.K. Jorgensen, R. Reisfeld, J. Less-Common Met. 93 (1983) 107.
[17] P. Porcher, in: R. Saez, P.A. Caro (Eds.), Rare Earths, Editorial Complutense, Madrid, 1998, p. 43.
[18] G.F. de Sá, W.M. de Azevedo, A.S.L. Gomes, J. Chem. Res. 6 (1994) 234.
[19] S.W. Kwon, S.B. Park, G. Seo, S.T. Hwang, J. Nucl. Mater. 257 (2) (1998) 172.
[20] Gallagher, McCarthy, Penn State University, University Park, PA, USA, ICDD Grant-in-Aid, 1973.