

Cerium-based phosphors: blue luminescent properties for applications in optical displays

Janaína Gomes · Osvaldo Antonio Serra

Received: 29 November 2006 / Accepted: 13 April 2007 / Published online: 28 June 2007
© Springer Science+Business Media, LLC 2007

Abstract In this paper, we describe the blue photoluminescence (PL) observed in the multi-component oxosalt phosphor $\text{GdVO}_4:\text{Ce}^{3+}$. Different doping concentrations (0.25–1 mol%) and heat treatment (900–1100 °C) were used to evaluate which conditions would lead to the most suitable blue phosphor for optimal display performance. The cerium doping concentration influences the profile of the emission spectrum (broad peak at 412 nm under UV excitation at 330 nm), as reflected on the values of chromaticity coordinates. On the basis of luminescent properties, we can conclude that, among the phosphors prepared in this work the most adequate for a blue display is the one obtained via the combustion method using glycine as fuel, a 0.50 mol% cerium doping concentration, and heat treatment at 1000 °C.

Introduction

Phosphor materials have found wide applications, which range from fluorescent lighting to luminescence immunoassay [1]. These materials essentially convert certain types of energy into electromagnetic radiation, usually in the visible range, and they should not absorb such radiation. Phosphors activated by rare earth (RE) ions exhibit some peculiarities. In the energy level diagram of RE ions,

luminescence processes often correspond to electronic transitions within the incompletely filled 4f shell, which is extensively shielded from the host lattice. Consequently, these phosphors have narrow band spectra in the visible region, which are to a great extent independent of the nature of the host lattice because of the low interaction between the RE and the crystal field. The luminescence quantum yield of phosphors activated with an RE ion is often high if compared with other phosphors [2]. Therefore, RE-doped phosphors play an important role in optical displays. In order to improve the performance of display devices, it is necessary to find novel blue phosphors with high luminescent efficiency and stability, which are lacking in the commercial area. Studies of GdVO_4 doped with RE ions such as Pr^{3+} , Nd^{3+} , Ho^{3+} , Eu^{3+} , Tm^{3+} , and Yb^{3+} have been reported [3–9] as laser medium. The strong absorption of ultraviolet light by GdVO_4 coupled with the effective energy transfer and strong emissions of VO_4^{3-} and Ce^{3+} should render a material that emits blue light very efficiently.

In this paper we describe the preparation of a highly luminescent blue-emitting Ce^{3+} -activated gadolinium vanadate phosphor obtained through a novel combustion synthesis technique. This method was chosen because it is known to yield fine particle sizes. The blue photoluminescence (PL) observed in the multi-component oxosalt phosphor $\text{GdVO}_4:\text{Ce}^{3+}$ is also reported here.

Experimental

Nanosized GdVO_4 consisting of $\text{Gd}(\text{NO}_3)_3$ (99.99%—Strem Chemicals) and $(\text{NH}_4)_3\text{VO}_4$ doped with 0.25, 0.50, and 1.00 mol% $\text{Ce}(\text{NO}_3)_3$ (99.995%—Aldrich) were prepared via the combustion synthesis procedure using

J. Gomes (✉) · O. A. Serra
Laboratório de Terras Raras – Departamento de Química –
Faculdade de Filosofia Ciências e Letras de Ribeirão Preto,
Universidade de São Paulo, Av Bandeirantes, 3900, Ribeirão
Preto, SP 14040-901, Brasil
e-mail: jangomes@usp.br

glycine as fuel. Post-annealing was performed for all the samples prepared as described above in muffle furnace for 4 h, at different heat treatment temperatures ranging from 900 to 1100 °C [10].

The crystalline structures of the phosphors were investigated by X-ray diffraction (XRD) on a SIEMENS D5000 diffractometer (K_{α} Cu radiation, $\lambda = 1.5418 \text{ \AA}$, graphite monochromator). The PL properties of the phosphors at room temperature were evaluated using a spectrofluorometer (FLUOROLOG3 ISA/Jobin-Yvon spectrofluorimeter, 450 W ozone-free Xenon lamp, Hamamatsu R928P photomultiplier). Scanning electron microscopy (SEM) was performed by using a Zeiss EVO 50 microscope. Samples prepared for SEM were first dispersed in acetone and dropped over a metallic holder, which was coated with a gold film, and a controlled deposition was achieved by using a Sputter Coater Baltec SCD 050.

Results and discussion

X-ray diffraction (XRD)

Representative $\text{GdVO}_4:\text{Ce}^{3+}$ samples were characterized by XRD. The patterns of the synthesized powders are shown in Fig. 1, where the influence of the annealing temperature on the phase formation can be noticed [12]. The majority of the detected reflection peaks can be assigned to the GdVO_4 crystalline phase; however, some of them correspond to Gd_2O_3 , present as an impurity phase. Although an increase in the post-annealing temperature

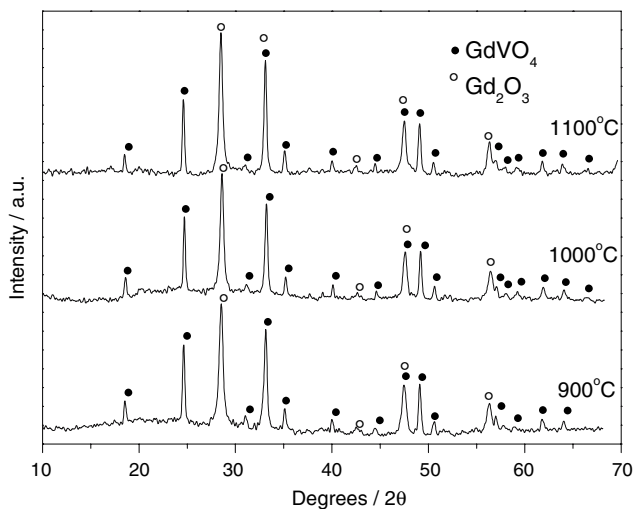


Fig. 1 XRD patterns recorded for $\text{GdVO}_4:\text{Ce}^{3+}$ prepared from precursors by the combustion method, using glycine as fuel and different heat treatments for 4 h, and a Ce^{3+} doping concentration of 0.50 mol%. PDF n. 86-0996, PDF n. 72-0277, PDF n. 17-0260 and PDF n. 76-0155 [11]

does not avoid the persistence of the oxide impurity in the material, it causes a sharpening of the reflection peaks. The method employed here probably also contributes to the formation of this impurity due to the temperature rate used throughout the combustion process.

The doping concentration also affects phase formation, as shown in Fig. 2. The presence of the Gd_2O_3 phase is predominant at Ce^{3+} doping concentrations of 0.50 mol% or above, which can be noted from the relative intensity of the reflection peaks in the different phases of the same sample. The presence of this Gd_2O_3 contaminating phase affects the intensity of the luminescence, as will be discussed in the section on emission spectra.

The crystallite sizes of all the samples were characterized by XRD. They were estimated from the half-width of the reflection peaks detected for the GdVO_4 single-phase only, by using the Scherrer's equation [13]. The average crystallite sizes of the $\text{GdVO}_4:\text{Ce}^{3+}$ samples, whose XRD are shown in Fig. 1, lie between 25–30 nm, indicating that the doping concentration influences this parameter (see Table 1).

Photoluminescence spectroscopy (PL)

Photoluminescence results were used to evaluate the optimum activator concentration and the best annealing temperature. This was done by comparing the qualitative emission intensity of all the spectra with those presented in Ref. [14] when preparing the desired phosphor. The typical PL emission intensity of the $\text{GdVO}_4:\text{Ce}^{3+}$ samples obtained under a 330 nm excitation is summarized in Fig. 3. By

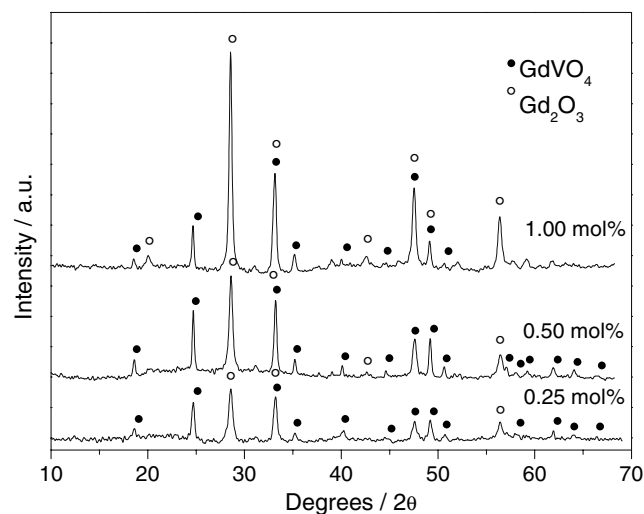


Fig. 2 XRD patterns recorded for $\text{GdVO}_4:\text{Ce}^{3+}$ prepared from precursor by the combustion method, using glycine as fuel and heat treatment at 1000 °C for 4 h. PDF n. 86-0996, PDF n. 72-0277, PDF n. 17-0260 and PDF n. 76-0155 [11]

Table 1 Determination of particle size and chromaticity coordinates for all phosphor samples

GdVO ₄ :Ce ³⁺ Samples		Particle size XRD (nm)	Chromaticity coordinates		
Activator concentration (mol%)	Post-annealing		X	Y	Z
0.25	900 °C	24	0.21	0.28	0.51
	1000 °C	24	0.20	0.30	0.50
	1100 °C	29	0.19	0.23	0.58
0.50	900 °C	29	0.18	0.15	0.68
	1000 °C	32	0.18	0.17	0.65
	1100 °C	31	0.17	0.17	0.66
1.00	900 °C	31	0.18	0.17	0.65
	1000 °C	30	0.19	0.17	0.64
	1100 °C	31	0.19	0.16	0.65

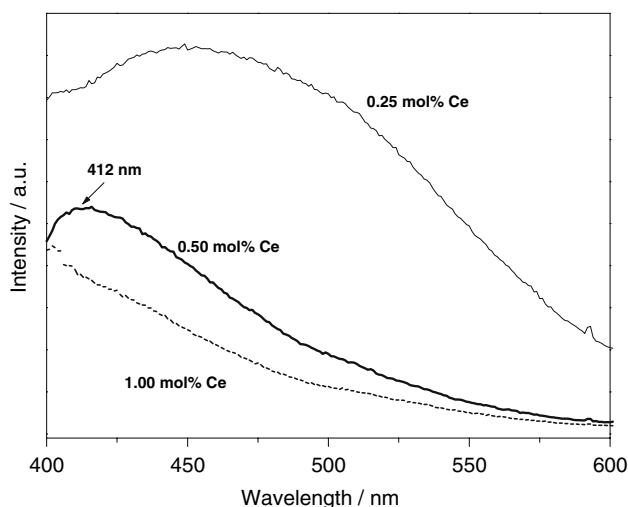


Fig. 3 Emission spectra at room temperature ($\lambda_{\text{ex}} = 330$ nm) of GdVO₄:Ce³⁺ prepared from precursor by the combustion method, using glycine as fuel and a post-annealing temperature of 1000 °C for 4 h

considering the concentration of each doping ion, the relative emission intensity was used to select the most intense luminescence obtained among the samples prepared under different post-annealing temperatures.

It can be seen from Fig. 3 that phosphors with emission centred in the blue region are obtained at an activator concentration of 0.50 mol%. Concentration quenching is also observed for all the samples. As for the emission intensity, it decreases with Gd₂O₃ phase formation, as observed in the diffractogram (XRD) patterns. The presence of this oxide phase allow us to control the broad emission of Ce³⁺, by reducing its emission to the blue region of the spectrum. This fact just occur due to the employed method (combustion method) that generates a rate of temperature and consequently the formation of a mixture among the desired oxosalt and the respective oxide.

Excitation in the UV region leads to two broad bands: at ~250 nm and ~315 nm, and a representative spectrum is shown in Fig. 4. These broad bands exhibit different behavior, depending on the concentration of the activator. At concentrations higher than 0.50 mol%, the band at 315 nm decreases, whereas the band at 250 nm increases in relative intensity, corroborating the quenching concentration observed in the emission spectra.

Chromaticity (CIE)

Basic requirements of phosphor displays are stability and purity of the emission color [15], according to a standard set by the EBU (European Broadcasting Union). Color purity can be visualized in the chromaticity diagram as blue, red and green regions, using the emission color coordinates of the luminescent material. So, from the luminescence emission spectra of some representative GdVO₄:Ce³⁺ samples we obtained their chromaticity diagrams and their respective chromaticity coordinates with

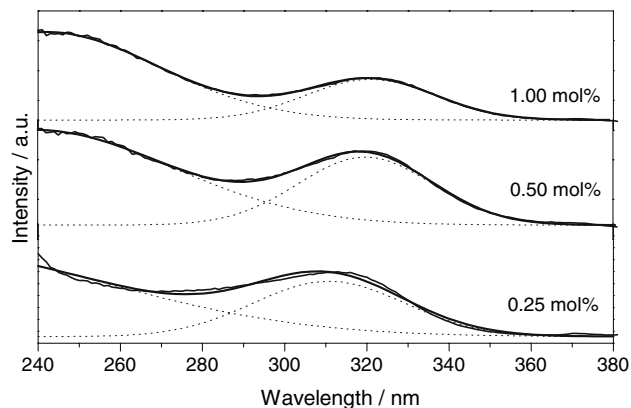


Fig. 4 Excitation spectra at room temperature ($\lambda_{\text{em}} = 412$ nm) of GdVO₄:Ce³⁺ prepared from precursor by the combustion method, using glycine as fuel and a post-annealing temperature of 1000 °C for 4 h

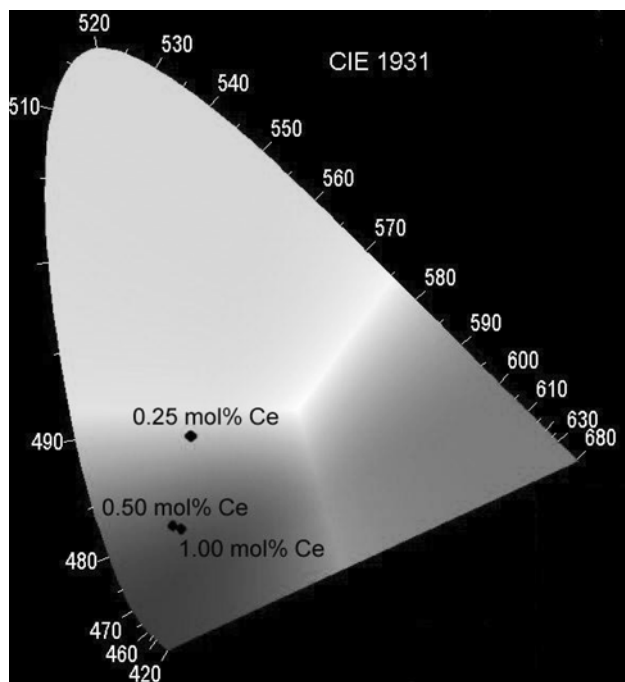
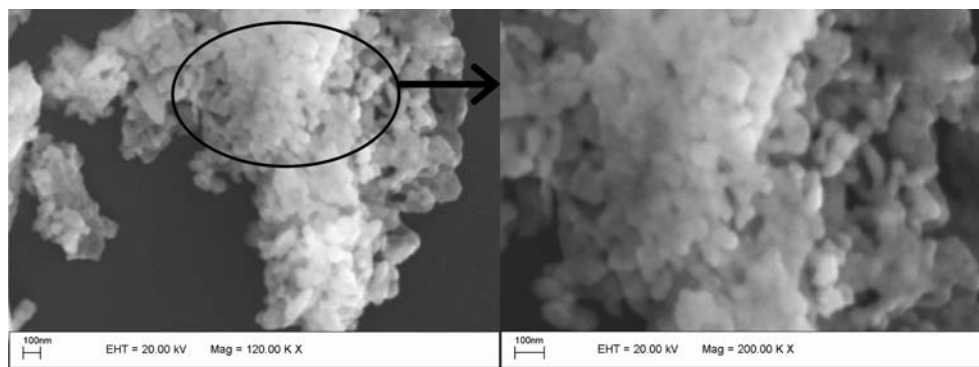


Fig. 5 Chromaticity diagram for the samples obtained at a heat treatment temperature of 1000 °C

the aid of the Spectra Lux Software v.2.0 Beta [16]. Figure 5 shows the chromaticity diagram obtained from the spectra with the most intense luminescence, recorded for samples prepared from different fuels. It can be seen that the sample obtained from glycine, doped with 0.50 mol% Ce^{3+} , and heat-treated at 1000 °C renders the most adequate color coordinates, Table 1, according to the EBU standard for a blue display phosphor ($y < 0.072$ and $x > 0.143$). For 0.50 and 1.00 mol% doping concentration the observed color is blue whereas for 0.25 mol%, the color is blue green.

Fig. 6 SEM of GdVO_4 with activator concentration 0.50 mol% Ce^{3+} and heat treatment at 1000 °C



Scanning electron microscopy (SEM)

The micrographs were obtained to evaluate the particle size and morphology of the powder. As can be observed in Fig. 6, the particle size is in agreement with Scherrer's equation, with a diameter in the range of 25–30 nm.

Conclusions

In summary, the synthesis of $\text{GdVO}_4:\text{Ce}^{3+}$ blue phosphors with broad PL emission was achieved at 1000 °C via the combustion method. Our results suggest that the phosphor obtained at lower heat treatment temperature (1000 °C) using glycine as fuel exhibits PL emission in the blue region (broad band centered at 412 nm) under UV excitation (330 nm). The diffraction peaks of this phosphor are well-defined, the particle size lies in the range of 25–30 nm, and it is formed by a mixture of two different phases, namely GdVO_4 and Gd_2O_3 . Comparing the luminescence intensities of the phosphors containing different activator concentrations, the material $\text{GdVO}_4:\text{Ce}^{3+}$ with a doping ion concentration of 0.50 mol% leads to the most intense luminescence. The chromaticity coordinates (0.18, 0.17, 0.65), dominant wavelength, and color purity of this phosphor are close to the values required for displays. Therefore, we can suggest that the combustion method is a promising technique for the preparation of blue phosphors for display technology.

Acknowledgments This work was financially supported by Fundação de Amparo à Pesquisa do Estado de São Paulo (FAPESP) Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq) and Coordenação de Aperfeiçoamento de Pessoal de Nível Superior (Capes).

References

1. Justel T, Nikol H, Ronda C (1998) *Angew Chem Int Ed* 37:3084
2. Blasse G, Grabmair BC (1994) In *Luminescent materials*, Springer Verlag, Berlin
3. Morris PJ, Lüthy W, Weber HP, Zavartsev YUD, Studenikin PA, Shcherbakov I, Zagumenyi AI (1994) *Opt Commun* 111:493
4. Zhang H, Meng X, Zhu L, Liu J, Wang C, Shao Z (1999) *Opt Laser Technol* 31:279
5. Zhang H, Meng X, Zhu L, Yang Z (1999) *Mater Res Bull* 34:1589
6. Zhang Q, Guo C, Shi C, Lü S (2000) *J Alloy Compd* 309:10
7. Hu X, Chen J, Zhuang N, Chen J, Lan J, Yang F (2003) *J Cryst Growth* 256:328
8. Xiong W, Lin S, Xie Y (2004) *J Cryst Growth* 263:353
9. Antic-Fidancev E, Lemaitre-Blaise M, Porcher P (1998) *Spectrochim Acta A* 54:2151
10. Gomes J, Pires AM, Serra OA (2004) *Quim Nova* 27:706
11. Powder Diffraction File PDF-2 database sets 1–44; Pennsylvania Joint Committee on Powder Diffraction Standards – International Center for Diffraction Data c 1998, (CD-ROM)
12. Minami T, Utsubo T, Miyata T, Suzuki Y (2003) *Thin Solid Films* 445:377
13. Cullity B (1978) In: *Elements of X-ray diffraction*, Addison Wesley, Redding, MA
14. Gomes J, Pires AM, Serra OA (2006) *J Fluoresc* 16:411
15. Justel T, Nikol H, Ronda C (1998) *Angew Chem Int Ed* 37:3084
16. Santa-Cruz PA, Teles FS, *Spectra Lux Software v.2.0 Beta*, Ponto Quântico Nanodispositivos 2003, RENAMI