Available online at www.sciencedirect.com

ScienceDirect

Optical Materials 29 (2007) 1852–1855

www.elsevier.com/locate/optmat

Highly enhanced luminescence of SrB_4O_7:Eu^{2+} phosphor prepared by the combustion method using glycine as fuel

Roberval Stefani [a], Alessandra de S. Maia [a], Cláudia A. Kodaira [b], Ercules E.S. Teotonio [a], Maria C.F.C. Felinto [b], Hermi F. Brito [a,*]

[a] *Instituto de Química, Universidade de São Paulo, C.P. 26077, CEP 05513-970, São Paulo – SP, Brazil*
[b] *Instituto de Pesquisas Energéticas e Nucleares, Av. Prof. Lineu Prestes 2242, CEP 05508-900, São Paulo – SP, Brazil*

Received 19 May 2006; received in revised form 25 July 2006; accepted 19 October 2006
Available online 4 December 2006

Abstract

Eu^{2+} ion doped into SrB_4O_7 matrix was prepared by combustion method heated at 900 °C in air, using urea (U) or glycine (G) as fuels in different ratios (U100, A10, A25, G10, G25, G75, and G100). In some compositions, ammonium acetate (AA) was used to reduce the exothermicity of combustion reaction. X-ray diffraction and luminescence spectroscopy were used to characterize the material. The high intense emission band at 367 nm is assigned to $4f^65d \rightarrow 4f^7(^8S_{7/2})$ transition arisen from divalent europium ion. It is observed that the interconfigurational transition is dependent on the molar ratio of glycine:urea fuels. Glycine fuel favors Eu^{2+} formation in SrB_4O_7 host lattice prepared by combustion method.

Keywords: Luminescence; Divalent europium; Strontium tetraborate; Glycine; Combustion method

---

1. Introduction

Phosphors are composed of an inert host lattice and an optically excited activator, typically of 3d or 4f metal ions. Usually, inorganic luminescent materials are applied in displays such as television tubes, computer monitor, oscilloscopes, radar screens and displays in electron microscopes [1]. The demands of these newer technologies have produced a search for new materials and synthesis techniques to improve the performance of inorganic luminescent phosphors. Phosphor powders are typically produced by solid-state reactions which require high temperatures and long reaction times. Their syntheses involve several steps such as raw material blending, high-temperature calcinations, washing, milling, classification (control of particle size), filtering, drying and sieving [2,3].

Combustion synthesis has been applied to phosphor preparation in the past few years and produces highly crystalline powders. Besides, it is an important powder processing technique generally used to produce complex oxide ceramics such as aluminates [4], ferrites, [5,6] and chromites [7]. The process involves exothermic reaction of an oxidizer such as metal nitrates, ammonium nitrate or ammonium perchlorate and an organic fuel, typically urea (CH_4N_2O), carbohydrazide (CH_6N_4O), or glycine ($C_2H_5NO_2$) [8].

The specific advantages using alternative preparation methods like combustion method are superior phase homogeneity, enhanced sinterability at a relatively low temperature, leading to microstructures with unique mechanical, electrical, dielectric, magnetic, and optical properties [9]. The reaction is self-sustaining, very vigorous and generates ultrafine nanoparticle powders, which have drawn great interest recently for their very attractive spectroscopic properties [10,11]. In addition, combustion method has the advantage of using a wide variety of fuels, rapid cooling leading to nucleation of crystallites without any growth

---

[*] Corresponding author.
E-mail address: hefbrito@iq.usp.br (H.F. Brito).

0925-3467/$ - see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.optmat.2006.10.012

and also has the potential to scale up [12]. Urea and, recently, glycine have been proven to be good fuels for the combustion method of a large number of materials [13,14].

In this work, we describe the improvement of the efficiency luminescence of the Eu^{2+} ion doped in strontium tetraborate matrix, using urea and glycine fuels in different molar ratios. In order to reduce the exothermicity of the combustion reaction, ammonium acetate was used together with urea in some fuel compositions [15]. The effect of these fuels in the solid properties was evaluated by X-ray diffraction (XRD) and photoluminescence spectroscopy.

2. Experimental

The precursor compounds used in this work were strontium nitrate (Synth), boric acid (Cinética Química), europium nitrate (prepared from Eu_2O_3, Aldrich, 99.9%), urea (Reagen), ammonium acetate (Merck), and glycine (Merck). An aqueous mixture containing stoichiometric amounts of reactants, 1% mol of $Eu(NO_3)_3 \cdot 6H_2O$ and fuel in the molar ratio of 2.5:1 to nitrate, was prepared and led to a muffle furnace heating from room temperature to 300 °C, using a heating rate of 3 °C/min to dehydrate and decompose. Then, in a few seconds, the mixture ignites, leading to smooth deflagration with enormous swelling, producing white foam. In this chemical reaction, NO_2, H_2O, NH_3, CO_2, O_2, and N_2 gases are released. The voluminous and foamy solid was milled and fired slowly at 400 °C for 1 h, then 500 °C for 1 h, yielding the precursor powder of $SrB_4O_7{:}RE^{2+}$. The final white powder was obtained by heating the precursor in alumina crucibles with lid at 700 °C for 1 h. The fuel compositions used during the experiments are given in Table 1. Finally, the samples were heating at 900 °C for 1 h to complete the phase formation.

XRD patterns of the powders were recorded on a Rigaku Miniflex diffractometer using Cu K_α radiation (30 kV and 15 mA) from 2 to 90° (2θ) and 1 s of pass time. Photoluminescence measurements were performed in a spectrofluorimeter SPEX-Fluorolog 2 with double grating 0.22 m monochromators (SPEX 1680), and a 450 W Xenon lamp as the excitation source. The excitation and emission spectra of $SrB_4O_7{:}Eu^{X+}$ ($X = 2$ or 3) systems were recorded at room and liquid nitrogen temperatures and collected at an angle of 22.5° (front face).

Table 1
Composition of the fuel mixtures used in combustion method to prepare $SrB_4O_7{:}Eu^{2+}$

Sample name	Fuel composition (%mol)
U100	100 U
A10	10 AA + 90 U
A25	25 AA + 75 U
G10	10 G + 90 U
G25	25 G + 75 U
G75	75 G + 25 U
G100	100 G

U: urea; AA: ammonium acetate; G: glycine.

3. Results and discussion

XRD patterns of some samples are shown in Fig. 1. As it can be seen, highly pure phase diffraction peaks of SrB_4O_7 are predominant in the XRD pattern of G100 sample. Most of intense reflections in XRD patterns of U100, G75, and G100 samples could be assigned to the tetraborate phase; however, in XRD patterns of A10, G10 and G25 samples, intense reflections from other phases are also observed [16]. Sr-metaborate (SrB_2O_4) is observed in the XRD pattern of G25 and G10 samples along with another not identified substance probably related to a polyborate with different SrO/B_2O_3 proportion (Fig. 1).

Excitation and emission spectra of the $SrB_4O_7{:}Eu^{2+}$ samples prepared by combustion method using urea and ammonium acetate compositions (U100, A10, and A25) recorded at 77 K are shown in Fig. 2. The emission spectra were also obtained at room temperature (Figure not shown) which present similar profiles as those recorded at 77 K indicating that there is no structural change with temperature lowering.

The excitation spectra under emission on the $4f^65d \rightarrow 4f^7$ ($^8S_{7/2}$) transition of Eu^{2+} ion, at 394 nm, display a broad band with maximum around 306 nm that corresponds to the $4f^7(^8S_{7/2}) \rightarrow 4f^65d$ transition (Fig. 2a). On the other hand, Fig. 2b shows emission spectra of these samples under excitation at 306 nm, which present broad bands in spectral range from 390 to 470 nm for the A25 and A10 samples assigned to interconfigurational $4f^65d \rightarrow 4f^7$ transitions of Eu^{2+} ion in different symmetry sites [17]. The U100 sample exhibits broad band assigned to these interconfigurational transitions split in three peaks

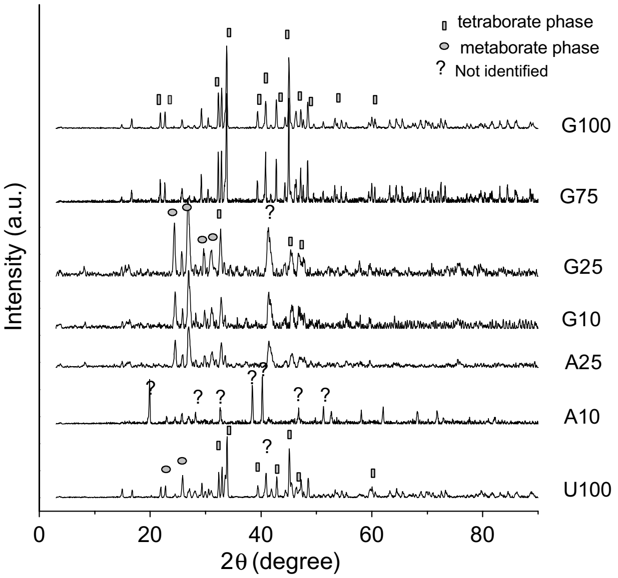

Fig. 1. X-ray diffraction patterns of $SrB_4O_7{:}Eu^{2+}$ system prepared by combustion method using different fuels.

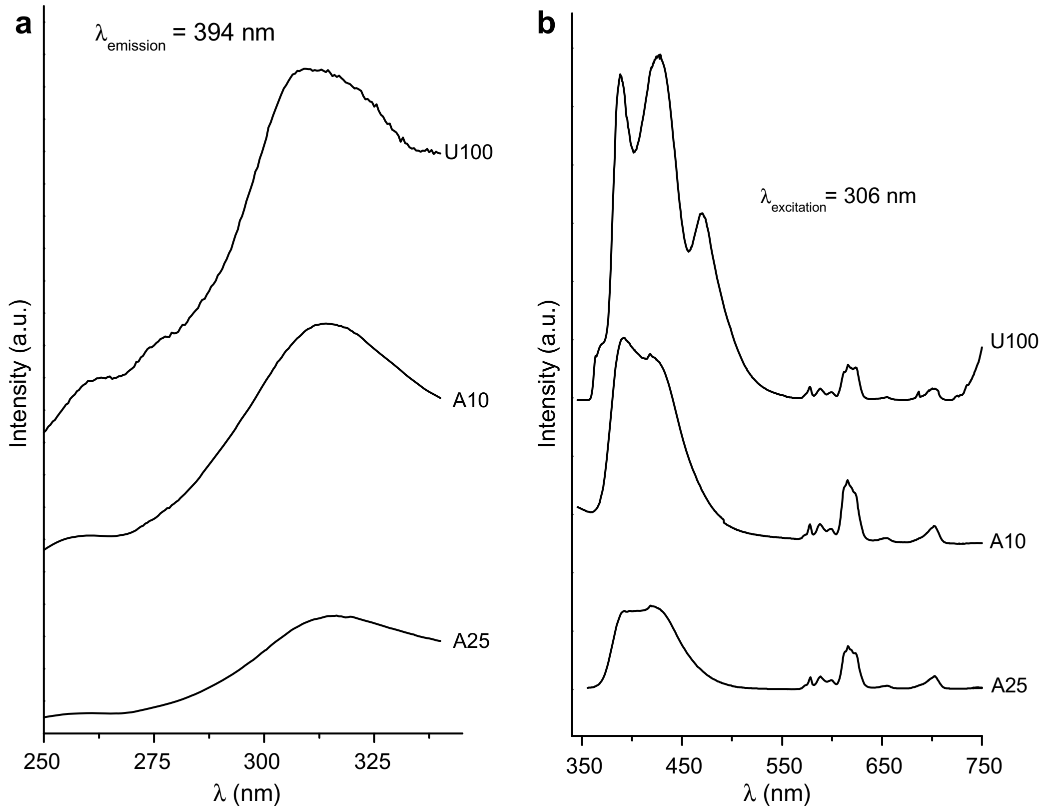

Fig. 2. Excitation (a) and emission (b) spectra of $SrB_4O_7:Eu^{2+}$ samples prepared by combustion method using ammonium acetate and urea fuel compositions recorded at 77 K.

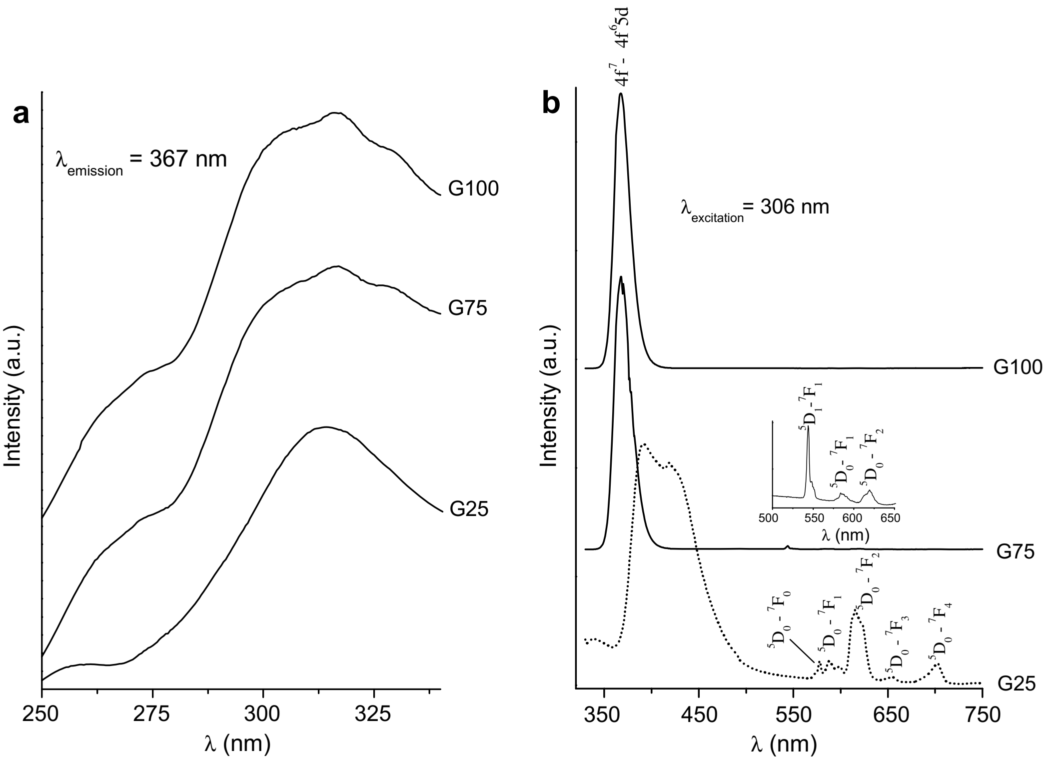

Fig. 3. Excitation (a) and emission (b) spectra of $SrB_4O_7:Eu^{2+}$ compound prepared with glycine and urea fuels recorded at 77 K.

at 388, 427, and 469 nm, which suggest that Eu^{2+} ion is also in different chemical environments. Besides, it is observed in the spectral range of 550–720 nm, the narrow intensity emission bands characteristic of $4f^6 \rightarrow 4f^6$ transitions attributed to $^5D_0 \rightarrow {}^7F_J$ transitions ($J = 0, 1, 2, 3, 4$) of Eu^{3+} ion [18,19]. According to these results, the reduction $Eu^{3+} \rightarrow Eu^{2+}$ was not efficient by addition of ammonium acetate as fuel. The charge compensation occurred probably by the presence of Sr^{2+} vacancies that appear in the compound when the Eu^{3+} ion occupies the Sr^{2+} site in the Srb_4O_7.

Fig. 3 shows the excitation and emission spectra of SrB_4O_7:Eu^{2+} samples using urea and glycine compositions (G25, G75 and G100) recorded at 77 K. The excitation spectra (Fig. 3a) exhibit broad band at 306 nm corresponding to $4f^7 \rightarrow 4f^65d$ transition of Eu^{2+} ion, under emission at 367 nm [17]. It is also observed weak emission peaks between 550 and 750 nm assigned to $^5D_0 \rightarrow {}^7F_J$ transitions ($J = 0$–4) from the Eu^{3+} ion [18,19]. Nevertheless, using high concentrations of glycine as fuel, the G75 and G100 samples present an intense broad band at 367 nm, which is assigned to $4f^65d \rightarrow 4f^7$ transition of divalent europium ion. These results are a good evidence that glycine is an efficient fuel for the $Eu^{3+} \rightarrow Eu^{2+}$ reduction. It is important to notice that the emission spectrum of G25 sample still presents the intraconfigurational transition indicating the presence of trivalent europium ion (inset Fig 3b). G25 (Fig. 3b), U100, A10, and A25 (Fig. 2b) samples display similar emission broad bands in the range of 350 and 500 nm attributed to Eu^{2+} ion present in different symmetry sites, while samples prepared using high concentration of glycine, G75 and G100 (Fig. 3b) present only one prominent emission band at around 367 nm related to an unique type of Eu^{2+} ion. This fact is corroborated by XRD patterns (Fig. 1), which show only one phase as for the G100 sample, while for the A10, G10, and G25 samples the presence of other phases are observed. The emission spectrum of G25 sample is observed two broad bands assigned to $4f^65d \rightarrow 4f^7$ transition of Eu^{2+} ion indicating that tetraborate and metaborate phase are dominant.

The emission bands of the G25 sample (Fig. 3) are assigned to the $Sr_{0.99}Eu_{0.01}B_2O_4$ in different phases. These data are in agreement with the those emission spectra reported by Machida et al. [20] that synthesized, characterized and studied the luminescent properties of $Sr_{0.99}Eu_{0.01}B_2O_4$ and Europium(II) metaborate. In that case, it was found other phases of $Sr_{0.99}Eu_{0.01}B_2O_4$ exhibiting relative emission bands with maxima at 367, 404, and 395 nm, which depend on preparation method at different temperatures.

4. Conclusion

Combustion method is a rapid and easy process to prepare borate phosphors doped with divalent europium ion. The conversion of Eu^{3+} to Eu^{2+} is irreversible therefore the system is air-stable. Although ammonium acetate reduces the exothermicity of the reaction leading to safer conditions, it difficults europium reduction. For the samples prepared using glycine and urea compositions as fuels, a partial conversion to Eu^{2+} is also observed. However, the preparation of SrB_4O_7:Eu^{2+} phosphors by combustion process using only glycine as fuel performed the complete conversion of Eu^{3+} to Eu^{2+} ions. Besides, these results show that luminescent inorganic materials with different optical properties can be obtained using different organic fuels. About the heat treatment, the principal advantage of this synthesis is to use the oxidizing atmosphere (air) instead reducing atmosphere. So, in this work it was not necessary the use of H_2/Ar gas for reducing.

Acknowledgements

The authors thank Conselho Nacional de Desenvolvimento Científico e Tecnológico (CNPq), Fundação de Amparo à Pesquisa do Estado de São Paulo (FAPESP), Rede de Nanotecnologia Molecular e de Interfaces (RENAMI) and Instituto do Milênio de Materiais Complexos (IM^2C) for financial support.

References

[1] C. Feldmann, T. Jüstel, C.R. Ronda, P.J. Smith, Adv. Funct. Mater. 13 (2003) 511.
[2] C.F. Bacalski, M.A. Cherry, G.A. Hirata, J. Mckittrick, J. Mourant, J. Soc. Inf. Display (Suppl-1) (2000) 93.
[3] G.C. Kim, H.L. Park, T.W. Kim, Mater. Res. Bull. 36 (2001) 1603.
[4] J.J. Kingsley, K. Suresh, K.C. Patil, J. Solid State Chem. 87 (1990) 435.
[5] K. Suresh, K.C. Patil, J. Solid State Chem. 99 (1992) 12.
[6] Y. Zhang, G.C. Stangle, J. Mater. Res. 9 (1994) 1997.
[7] L.A. Chick, L.R. Pederson, G.D. Maupin, J.L. Bates, L.E. Thomas, G.J. Exarhos, Mater. Lett. 10 (1990) 6.
[8] J.J. Kingsley, K. Suresh, K.C. Patil, J. Mater. Sci. 25 (1990) 1305.
[9] C. Suryanarayana, Bull. Mater. Sci. 17 (1994) 307.
[10] R.N. Bhargava, J. Lumin. 72–74 (1997) 46.
[11] L. Sun, J. Yao, C. Liu, C. Liao, C. Yan, J. Lumin. 87–89 (2000) 447.
[12] K.C. Patil, S.T. Aruna, S. Ekambaram, Curr. Opin. Solid State Mater. Sci. 2 (1997) 158.
[13] M.W. Murphy, T.R. Armstrong, P.A. Smith, J. Am. Ceram. Soc. 80 (1997) 165.
[14] L.E. Shea, J. McKittrick, O.A. Lopez, E. Sluzki, J. Am. Ceram. Soc. 79 (1996) 3257.
[15] T. Aruna, K.S. Rajam, Mater. Res. Bull. 39 (2004) 157.
[16] A. Lavat, C. Graselli, M. Santiago, J. Pomarico, E. Caselli, Cryst. Res. Technol. 39 (2004) 840.
[17] P. Dorenbos, J. Lumin. 104 (2003) 239.
[18] E.E.S. Teotonio, M.C.F.C. Felinto, H.F. Brito, O.L. Malta, A.C. Trindade, R. Najjar, W. Strek, Inorg. Chim. Acta 357 (2004) 451.
[19] R. Stefani, A.D. Maia, E.E.S. Teotonio, M.A.F. Monteiro, M.C.F.C. Felinto, H.F. Brito, J. Solid State Chem. 179 (2006) 1075.
[20] K. Machida, G. Adachi, J. Shiokawa, M. Shimada, M. Koizumi, Inorg. Chem. 19 (1980) 983.