Photoluminescent behavior of $SrB_4O_7{:}RE^{2+}$ (RE = Sm and Eu) prepared by Pechini, combustion and ceramic methods

R. Stefani[a], A.D. Maia[a], E.E.S. Teotonio[a], M.A.F. Monteiro[a], M.C.F.C. Felinto[b], H.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, Cidade Universitária, São Paulo-SP, Brazil

Abstract

This work reports the preparation of system containing RE^{2+} ions (RE = Sm and Eu)-doped in SrB_4O_7 matrix by ceramic, Pechini and combustion methods. These compounds were prepared by reduction of RE^{3+} to RE^{2+} in air, which exhibit some different features according to the preparation method. Photoluminescent properties of these systems were investigated based on the emission and excitation spectral data. The emission spectra of $SrB_4O_7{:}Eu^{2+}$ system prepared by combustion and Pechini methods are characterized by a broad band assigned to interconfigurational $4f^65d{\rightarrow}4f^7$ transition, while $SrB_4O_7{:}Sm^{2+}$ compound exhibit narrow emission bands arising from intraconfigurational-$4f^6$ also shows $^4G_{5/2}{\rightarrow}^6H_{J'}$ transitions ($J' = \frac{5}{2}, \frac{7}{2}, \frac{9}{2}$ and $\frac{11}{2}$) arising from Sm^{3+} ion, transitions. $SrB_4O_7{:}RE$ system prepared by combustion method presents emission bands from RE^{3+} ions as intense as that arising from RE^{2+}, suggesting that the preparation route is not efficient for the reduction $RE^{3+}{\rightarrow}RE^{2+}$ process. Emission quantum efficiency and radiative emission rates of Sm^{2+} ion are determined and discussed.
© 2006 Elsevier Inc. All rights reserved.

Keywords: Luminescence; Borates; Divalent rare earths; Luminescence; *f–d* transitions

1. Introduction

In recent years, the versatility of efficient luminescent materials have attracted researchers' attention due to their applications in the field of fluorescent lamps, display devices, detector systems represented by X-ray screens, immunoassays and scintillates of phosphor marking [1–4]. Borate systems have proved to be potential candidates for aforementioned applications [4,5]. For example, strontium tetraborate (SrB_4O_7) has been investigated as a potential non-linear optical material with some excellent mechanical and optical properties such as high mechanical strength, non-hygroscopicity and high optical damage threshold [6].

Eu^{2+} and Gd^{3+} ions ($4f^7$-configuration) present $^8S_{7/2}$ and $^6P_{7/2}$ levels as ground and excited states, respectively.

Consequently, a qualitative interpretation of intraconfigurational transitions can be made in a similar way, but the position of excited $^6P_{7/2}$ level of Eu^{2+} ion is at a lower energy ($\sim 28{,}000 \, cm^{-1}$) than Gd^{3+} ions ($\sim 32{,}000 \, cm^{-1}$). This behavior is also observed for Sm^{2+} and Eu^{3+} ions that present $4f^6$-configuration where the first excited $^5D_0$ level is around 14,500 and 17,300 cm^{-1}, respectively. Fig. 1 shows partial energy level diagram of free Sm^{2+}, Sm^{3+}, Eu^{2+}, Eu^{3+} and Gd^{3+} ions including the lowest energy f–d levels [7–10].

The most important characteristic of divalent europium ion is that, it shows broad emission bands, in visible spectrum, arising from interconfigurational $4f^7$–$4f^65d^1$ transitions which are strongly dependent on chemical environment since $5d$ orbitals have a great radial extension and are more sensitive to the ligand field [11–13]. Accordingly, f–d emission bands can be shifted from blue to red region, which makes Eu^{2+} ion potentially promising

---

*Corresponding author. Fax: +55 11 3815 5579.
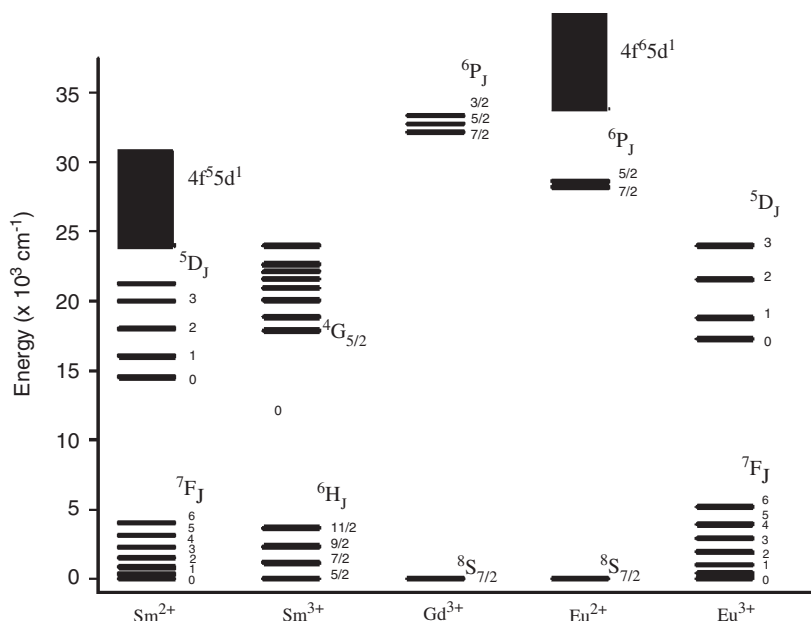*E-mail address:* hefbrito@iq.usp.br (H.F. Brito).

Fig. 1. Partial energy level diagram of free divalent and trivalent rare earth ions (Sm^{2+}, Sm^{3+}, Eu^{2+}, Eu^{3+} and Gd^{3+}) containing the lowest energy f–d levels.

systems as phosphors for applications in displays, lamps and luminescent paintings used for several signs and directions, meaning to provide safe traffic, road markers and important devices.

On the other hand, emission spectra of divalent samarium ions, in the spectral range from 770 to 800 nm, are generally dominated by narrow bands that are assigned to the intraconfigurational ($4f^6$–$4f^6$) transitions. The presence of these sharp bands is due to $4f$ electrons that are well protected from ligand field by $5s^2 5p^6$ external orbitals and band positions are only slightly affected by environment around samarium ion [13].

Solid state systems containing divalent rare earth ions have been prepared using reducing agents such as H_2 to reduce RE^{3+} to RE^{2+} ions. However, some RE^{2+}-systems can also be prepared by reduction process of RE^{3+} ion using solid state reaction at high temperature in air and/or N_2 atmospheres. For example, the Eu^{3+} or Sm^{3+} ions doped into SrB_4O_7 were reduced to their corresponding divalent rare earth ions by a solid state reaction at high temperature in air [14]. The ease of incorporation and stabilization of Eu^{2+} and Sm^{2+} ions in this material is due to unique structure of SrB_4O_7 matrix considering that all boron atoms are tetrahedrally coordinated forming a three-dimensional $(B_4O_7)_\infty$-network by corner-sharing, containing channels parallel to b-axis. The strontium ion fits into these channels and is surrounded by nine oxygen atoms, giving SrO_9 polyhedral, with C_s symmetry. Divalent rare earth ions are therefore located in a "cage" formed by BO_4 unit from $(B_4O_7)_\infty$-network with rigid structure which prevents oxidation of RE^{2+} to RE^{3+} ions [15].

The purpose of this work is to investigate photoluminescence properties of Eu^{2+} and Sm^{2+} doped in SrB_4O_7 host

systems prepared by Pechini [16] and combustion [17] as alternative methods, in milder experimental conditions than the solid state reaction (ceramic method) [18]. Luminescent behavior of Sm^{2+} and Eu^{2+} ions in this matrix were investigated based on intra and interconfigurational transitions. Experimental quantum efficiencies (η) for the emitting $^5D_0$ level of Sm^{2+} ion were determined and discussed.

2. Experimental

The preparation of SrB_4O_7:RE^{2+} system ($RE = Sm$ and Eu) by ceramic method was carried out in air. Stoichiometric amounts of $Sr(NO_3)_2$ (Synth) and H_3BO_3 (Cinética Química) together with a 3 mol% excess of H_3BO_3 to compensate for B_2O_3 evaporation were thoroughly mixed and grounded. The dopant concentration of RE^{3+} added as $RE(NO_3)_3 \cdot 6H_2O$ (prepared from Eu_2O_3, Aldrich, 99.9%), was 1 mol% of Sr^{2+} ion concentration in host compound. The mixtures were heated in air at 700 °C in alumina crucibles for 5 h and then grounded and heated at 850 °C for another 5 h. The second heating step was repeated once.

In preparation by Pechini method, the stoichiometric quantities of $Sr(NO_3)_2$, $RE(NO_3)_3 \cdot 6H_2O$ (1 mol% of Sr^{2+}) and H_3BO_3 precursors were dissolved in deionized water. In this solution, preheated at 70 °C, citric acid was added in molar ratio of 3:1 (citric acid:Sr^{2+}) and ethylene glycol in weight ratio of 3.6:1 (citric acid:ethylene glycol) under stirring. Then, this mixture was heated at 110 °C, and the formation of brown transparent glassy polymeric resin was observed. After, the resin was heated at 300 °C for 2 h, resulting in a fluffy black mass, which was grounded into a powder. Finally, this material was calcinated at different

temperatures and times and the optimized condition was obtained by heating at 900 °C during 3 h, which produced a SrB_4O_7:Sm^{2+} powder sample.

For the system prepared by combustion method, similar molar quantities of reagents to traditional ceramic method were used. Urea in 2.5 mol% of Sr^{2+} was used as combustible, which was added to mixture of rare earth and strontium nitrates and boric acid dissolved in deionized water. The resultant solution was heated at 300 °C (3 °C/min) in the hot plate 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 2 h, yielding the precursor powder of SrB_4O_7:RE^{2+}. Thermal treatment was performed at different temperatures, but the final powder was only obtained after heating at least at 700 °C for 2 h.

The purity and compositions of the samples were checked by X-ray diffraction (XRD) patterns recorded on a Philips diffractometer model X'Pert-MPD using Cu$K\alpha$ radiation (40 kV and 40 mA) in the interval of 2–70° (2θ) and 1 s of pass time, using the powder XRD method.

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 excitation source. A spectroscopy computer DM3000F controlled this apparatus. The excitation and emission spectra at room and liquid nitrogen temperatures were collected at an angle of 22.5° (front face).

The infrared absorption spectra were recorded in KBr pellets on a Bomen Model MB-100 spectrophotometer in the range of 4000–400 cm^{-1}.

The media crystallite size of the samples was determined using the Scherrer's formula [19].

3. Results and discussion

IR spectra of the samples are presented in Fig. 2. The spectra of the systems prepared by ceramic and Pechini methods exhibit very similar profiles, showing that the exact positions of all the prominent bands in the host borates spectra are coincident. It is also important to report that these spectra present characteristic bands centered at 1100 cm^{-1}, which are associated to tetrahedrally coordinated B atoms [20]. This result indicates that the same type of system was obtained in spite of the preparation method. On the other hand, the samples prepared by combustion method exhibit IR spectra with additional bands (above 1100 cm^{-1}), which are assigned to BO_3-trigonal group in metaborate phase. These results are confirmed by the powder XRD patterns of SrB_4O_7:RE^{2+} shown in Fig. 3. For example, it is observed that, when ceramic and Pechini methods are used, most of intense reflections are assigned to the tetraborate phase [21], while a very low proportion of tetraborate is observed when the samples are prepared by the combustion method where metaborate phase is the foremost one. It is important to report that no significant difference was observed in the IR and powder XRD patterns for SrB_4O_7:RE^{2+} compound obtained by combustion method under heating at 700, 850 and 900 °C. This result gives good evidence that the same product was obtained at different temperatures.

Average crystallite size of samples prepared by different methods was determined using Scherrer's formula [19]. Values of particle sizes of divalent samarium and europium ions are 81 and 79 nm, prepared by ceramic method, 77 and 67 nm by Pechini method and 38 and 39 nm by combustion method, respectively. These results show that average particle sizes of SrB_4O_7:RE^{2+} system prepared by combustion method are almost twice smaller than those synthesized by ceramic and Pechini methods.

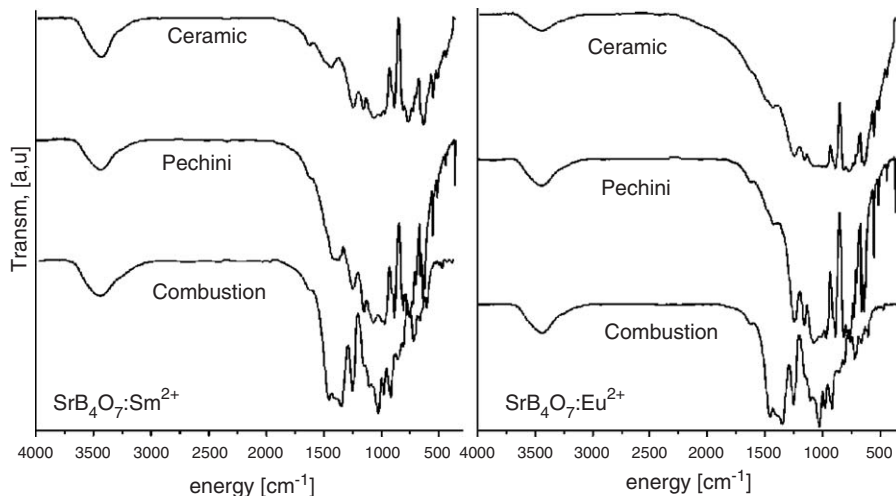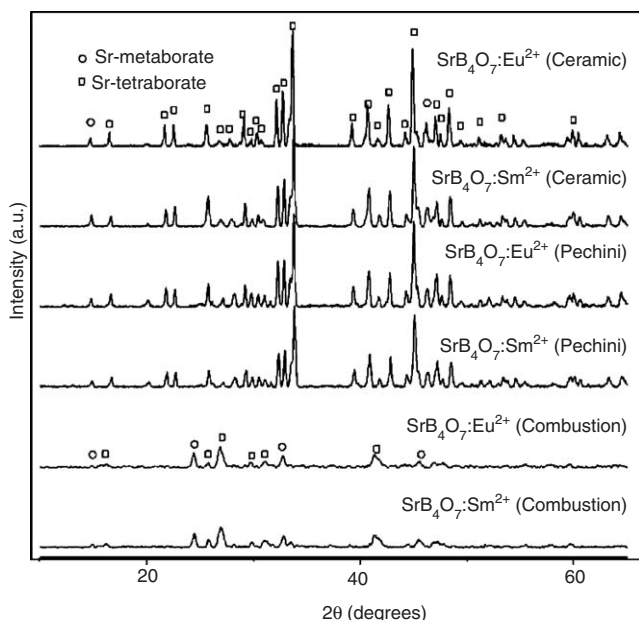Fig. 2. Infrared spectra of SrB_4O_7:RE^{2+} (Sm and Eu) systems prepared by ceramic, Pechini and combustion methods.

Fig. 3. X-ray diffraction patterns of $SrB_4O_7:RE^{2+}$ (Sm and Eu) systems prepared by Pechini, combustion and ceramic methods at 900, 700 and 850 °C, respectively.

3.1. Photoluminescence investigation

Excitation spectra of $SrB_4O_7:Sm^{2+}$ samples prepared by ceramic, Pechini and combustion methods recorded at 77 K are shown in Fig. 4a–c. These spectra were recorded monitoring the emission intensity of intraconfigurational $^5D_0 \rightarrow {}^7F_0$ transition (around 685 nm) centered on Sm^{2+} ion. Generally, spectra of Sm^{2+} systems display broad bands in spectral range of 250–550 nm corresponding to interconfigurational $4f^6 \rightarrow 4f^5 5d$ transition, presenting two split components t_{2g} and e_g of 5d excited state from rare earth ion. A number of sharp peaks due to crystal-field interaction of $4f^5$ are also observed. When a comparison is made among excitation spectra of $SrB_4O_7:Sm^{2+}$ samples prepared by different methods, it is observed that samples prepared by ceramic and Pechini methods show similar excitation spectral profiles (Figs. 4a and b). On the other hand, excitation spectra of Sm^{2+}-samples prepared by combustion method exhibit an intense band around 280 nm which may be assigned to transitions of Sm^{3+} ion (Fig. 4c), since this ion was not totally converted to Sm^{2+} ion as a consequence of the presence of metaborate phase.

Figs. 4d–f exhibit emission spectra of Sm-samples recorded at 77 K with excitation monitored at 367 nm. These spectra present narrow emission bands in the range from 680 to 775 nm, that are attributed to intraconfigurational $^5D_0 \rightarrow {}^7F_J$ transitions (J = 0, 1, 2 and 3) arising from Sm^{2+} ion (Table 1). These transitions are split in a maximum of $(2J + 1)$-components suggesting the presence of only one site of symmetry around the divalent samarium ion. Furthermore, the emission spectrum of Sm-sample prepared by combustion method also shows $^4G_{5/2} \rightarrow {}^6H_{J'}$

transitions ($J' = \frac{5}{2}, \frac{7}{2}, \frac{9}{2}$ and $\frac{11}{2}$) arising from Sm^{3+} ion, which indicates only a partial conversion to Sm^{2+} ion and suggests a very low proportion of tetraborate phase. Since the excitation is monitored on interconfigurational $4f^6 \rightarrow 4f^5 5d$ transition, the absence of broad band from emission spectra is an indicative of an efficient energy transfer from the states of $4f^5 5d$ configuration to excited levels of Sm^{2+} ion.

It is important to report that the emission spectra of all Sm-samples also exhibit narrow bands arising from $^5D_1 \rightarrow {}^7F_J$ transitions in spectral range 620–675 nm. However, their intensities are higher when spectra were recorded at 77 K than at room temperature. This result is a consequence of the small energy gap between $^5D_0$ and $^5D_1$ excited states ($\Delta E \approx 1350 \text{ cm}^{-1}$), which is very close to vibration mode of BO_4 around 1300 cm^{-1}. Thus emission bands from $^5D_1$ excited level may be explained by a thermal population of $^5D_1$ level from $^5D_0$ state.

Luminescence decay curves of $SrB_4O_7:Sm^{2+}$ system were recorded monitoring emission on $^5D_0 \rightarrow {}^7F_0$ transition (~685 nm) and excitation at 367 nm, at room temperature. The decay curves for all samples present mono-exponential behavior with similar values of lifetimes for the emitting $^5D_0$ level (Table 2). These data are in accordance with the presence of only one non-radiative deactivation channel acting on the emitting level $^5D_0$.

Photoluminescence properties of $SrB_4O_7:RE$ (RE = Sm and Eu) systems were investigated based on excitation and emission spectra recorded at room and at liquid nitrogen temperatures. All spectra recorded at low temperature are similar profiles to those obtained at room temperature, however presenting better resolution.

In order to investigate spectroscopic properties of Sm^{2+} doped in SrB_4O_7 host, the transition probabilities for zero-phonon lines and emission quantum efficiency were determined. The spontaneous emission coefficients A_{0J} for $^5D_0 \rightarrow {}^7F_J$ transitions were determined in a similar procedure used for Eu^{3+} ion [20,21], by taking magnetic dipole $^5D_0 \rightarrow {}^7F_1$ transition as standard, since the emission probability of this transition is practically insensitive to chemical environment around Eu^{3+} and Sm^{2+} ions (Eu^{3+}, $A_{01} = 50 \text{ s}^{-1}$ and Sm^{2+}, $A_{01} = 29 \text{ s}^{-1}$). The emission coefficients were determined by following equation [22]:

$$A_{0\lambda} = A_{01} \left(\frac{S_{0\lambda}}{S_{01}} \right) \left(\frac{\sigma_{01}}{\sigma_{0\lambda}} \right), \tag{1}$$

where $S_{0\lambda}$ and $\sigma_{0\lambda}$ are the area under the emission band and the energy barycenter of $^5D_0 \rightarrow {}^7F_\lambda$ transition, respectively. By the relation between the lifetime of $^5D_0$ emitting state and total decay rate ($1/\tau = A_{rad} + A_{nrad}$), where A_{rad} and A_{nrad} are the radiative and non-radiative rates, respectively, the value can be calculated by following equation [23]:

$$\eta = \frac{A_{rad}}{A_{rad} + A_{nrad}}. \tag{2}$$

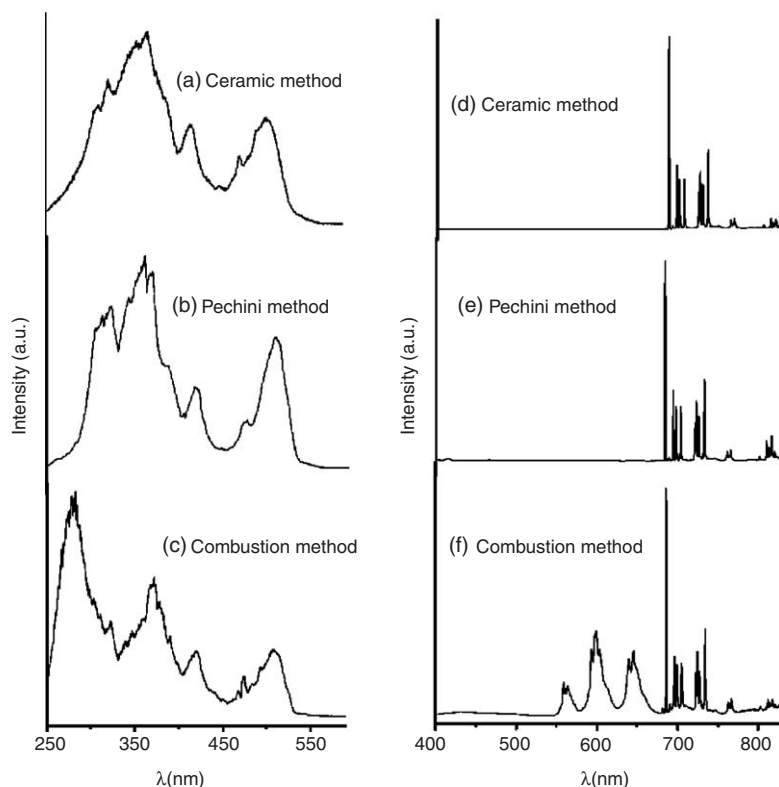Table 2 presents the experimental intensity parameter for $SrB_4O_7:Sm$ compound prepared by the three different

Fig. 4. Luminescence spectra of SrB_4O_7:Sm^{2+} system prepared by ceramic, Pechini and combustion methods: (a) excitation spectra recorded with emission monitored around 685 nm and (b) emission spectra recorded under excitation at 350 nm.

Table 1
Transition energies of $^5D_0 \rightarrow ^7F_J$ manifolds (in cm^{-1}) observed in the emission spectra of SrB_4O_7:Sm^{2+} samples, at 77 K

Transitions	Preparation methods		
	Ceramic	Pechini	Combustion
$^5D_0 \rightarrow ^7F_0$	14,585	14,587	14,590
	14,376	14,378	14,380
$^5D_0 \rightarrow ^7F_1$	14,310	14,306	14,310
	14,188	14,194	14,192
	13,846	13,840	13,846
$^5D_0 \rightarrow ^7F_2$	13,808	13,812	13,808
	13,751	13,755	13,751
	13,627	13,623	13,627
$^5D_0 \rightarrow ^7F_3$	13,140	13,131	13,113
	13,044	13,046	13,041
	12,465	12,493	12,456
	12,330	12,358	12,315
$^5D_0 \rightarrow ^7F_4$	12,291	12,318	12,282
	12,240	12,264	12,228
	12,186	12,216	12,183

preparation methods. As it can be seen, quantum emission efficiency of emitting $^5D_0$ level is around 37% suggesting that these compounds present great potential for application as phosphors. Besides, no significant change in the η values has been observed when the particles sizes were changed. An important feature to be observed is the higher values of R_{02} parameter, which is given by the integral ratio between the intensities. The values of R_{02} for Sm^{2+}-systems around 0.7 are higher than those obtained for Eu^{3+} compounds, suggesting that there is a higher J-mixing in the Sm^{2+}-systems.

The luminescence properties of SrB_4O_7:Eu^{2+} compound were investigated based on excitation and emission spectral data. Figs. 5a–c show excitation spectra of europium samples recorded at 77 K by monitoring emission of Eu^{2+} ion ($4f^65d \rightarrow 4f^7$ transition) at 367 nm. It is clearly stated that these spectra display mainly two broad bands with maxima around 270 and 310 nm that correspond to splitting of $5d$ orbital in t_{2g} and e_g components.

Figs. 5d–f show emission spectra of Eu^{3+}-doped SrB_4O_7 under excitation at 265 nm. The main features of the spectra of compounds prepared by Pechini and ceramic methods (Figs. 5d and e) present broad bands around 367 nm, which is assigned to interconfigurational transition $4f^7 \rightarrow 4f^65d$ arising from Eu^{2+} ion. It is also observed very weak emission bands in 570–720 nm spectral range, corresponding to intraconfigurational $^5D_0 \rightarrow ^7F_J$ transitions ($J = 0, 1, 2, 3, 4$) centered on Eu^{3+} ion [23]. This result is a good evidence of the efficient reduction $Eu^{3+} \rightarrow Eu^{2+}$ process. On the other hand, the sample prepared by combustion method (Fig. 5f) exhibits emission spectrum with transition $^5D_0 \rightarrow ^7F_J$ (Eu^{3+}) as intense as that arising

Table 2
Emission quantum efficient (η), lifetimes (τ) and radiative decay rates (A_{rad}), non-radiative (A_{nrad}) and total (A_{total}) for $SrB_4O_7:Sm^{2+}$ system prepared by ceramic, Pechini and combustion methods

$SrB_4O_7:Sm^{2+}$	A_{rad} (s^{-1})	A_{nrad} (s^{-1})	A_{total} (s^{-1})	R_{0-2}	τ (ms)	η (%)
Ceramic	100	175	275	0.736	3.627	36
Pechini	118	194	312	0.690	3.196	37
Combustion	120	202	322	0.524	3.100	37

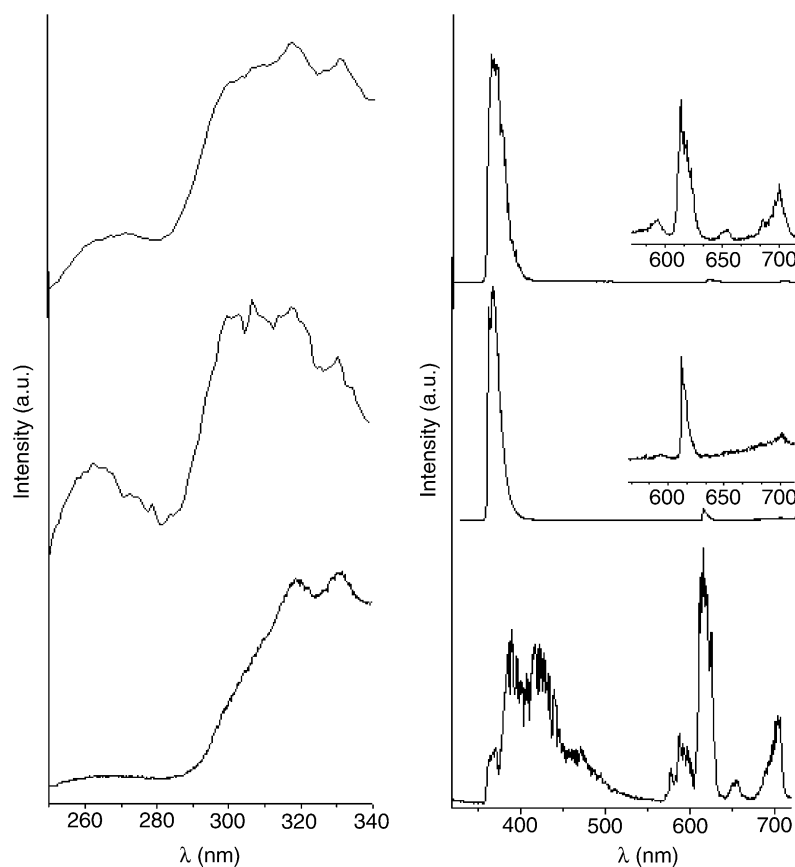Fig. 5. Luminescence spectra of $SrB_4O_7:Eu^{2+}$ system prepared by ceramic, Pechini and combustion methods: (a) excitation spectra recorded with emission monitored around 367 nm and (b) emission spectra recorded with excitation monitored around 265 nm.

from $4f^65d \rightarrow 4f^7$ transition (Eu^{2+}), indicating that the reduction process is incomplete. Similarly to samarium systems this behavior may be explained as a consequence of the structural change, suggesting a very low proportion of tetraborate phase.

4. Conclusions

$SrB_4O_7:RE$ system prepared by ceramic and Pechini methods exhibits emission bands arising from Sm^{2+} and Eu^{2+} ions, suggesting an efficient reduction process from RE^{3+} to RE^{2+}. While the $SrB_4O_7:RE$ system prepared by combustion method exhibits emission bands from RE^{3+} ions suggesting that the reduction $RE^{3+} \rightarrow RE^{2+}$ process was incomplete.

Sm-samples present narrow emission bands attributed to intraconfigurational $^5D_0 \rightarrow {}^7F_J$ transitions of Sm^{2+} ion except for the sample prepared by combustion method that also shows $^4G_{5/2} \rightarrow {}^6H_J$ transitions of Sm^{3+} ion. In case of Eu^{3+}-doped SrB_4O_7 prepared by Pechini and ceramic methods present emission broad bands assigned to inter-configurational transition $4f^65d \rightarrow 4f^7$ arising from Eu^{2+} ion when compared with combustion method. Based on optical data of $SrB_4O_7:RE^{2+}$, it is observed that the reduction of $RE^{3+} \rightarrow RE^{2+}$ is more efficient for the system prepared by ceramic and Pechini methods than that by combustion. This result may be explained as a consequence of preferential metaborate phase for the $SrB_4O_7:RE^{2+}$ systems when they were obtained by combustion method.

References

[1] B. Lei, Y. Liu, J. Liu, Z. Ye, C. Shi, J. Solid State Chem. 177 (2004) 1333.

[2] T. Matsuzawa, Y. Aoki, N. Takeuchi, Y. Murayama, J. Eletrochem. Soc. 143 (1996) 2670.

[3] W.O. Gordon, J.A. Carter, B.M. Tissue, J. Lumin. 108 (2004) 339.

[4] G. Bertrand-Chadeyron, M. El-Ghozzi, D. Boyer, R. Mahiou, J.C. Cousseins, J. Alloys Compd. 317 (2001) 183.

[5] A. Diaz, D.A. Keszler, Mater. Res. Bull. 31 (1996) 147.

[6] Y.U. Oseledchik, A.L. Prosvirnin, V.V. Starshenko, V.V. Osadchuk, A.I. Pisarevsky, S.P. Belokrys, A.S. Korol, N.V. Svitanko, A.F. Selevich, S.A. Krikunov, J. Cryst. Growth 135 (1994) 373.

[7] P. Dorenbos, J. Lumin. 104 (2003) 239.

[8] W.C. Martin, R. Zalubas, L. Hagan, Atomic Energy levels—The Rare-Earth Elements, National Bureau of Standards, US government Printing Office, Washington, 1978.

[9] H.F. Brito, G.K. Liu, J. Chem. Phys. 112 (2000) 4334.

[10] W.T. Carnall, G.L. Goodman, K. Rajnak, R.S. Rana, J. Chem. Phys. 90 (1989) 3443.

[11] J.M. Rey, J.R.G. Thorne, R.G. Denning, H. Bill, J. Phys.: Condens. Matter 17 (2005) 1861.

[12] M.F. Reid, L. van Pieterson, A. Meijerink, J. Alloys Compd. 344 (2002) 240.

[13] L. Ning, C. Duan, S. Xia, M.F. Reid, P.A. Tanner, J. Alloys Compd. 366 (2004) 34.

[14] Z. Pei, Q. Su, J. Zhang, J. Alloys Compd. 198 (1993) 51.

[15] K. Machida, G. Adachi, J. Shiokawa, Acta Crystallogr. B 36 (1980) 2008.

[16] M.U. Pechini, US Patent No. 3330697, 1967.

[17] S. Shikao, W. Jiye, J. Alloys Compd. 327 (2001) 82.

[18] G.Y. Adachi, K.I. Machida, J. Shiokawa, J. Less-Common Met. 93 (1983) 389.

[19] B.D. Cullity, Elements of X-ray Diffraction, Addion-Wesley Publishing Company Inc., Reading, MA, 1967.

[20] P.B. Hart, S.E.F. Smallwood, J. Inorg. Nucl. Chem. 24 (1962) 1047.

[21] A. Lavat, C. Graselli, M. Santiago, J. Pomarico, E. Caselli, Cryst. Res. Technol. 39 (2004) 840.

[22] C.A. Kodaira, H.F. Brito, O.L. Malta, O.A. Serra, J. Lumin. 101 (2003) 11.

[23] 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.