

## Deep Red Color Emission in $\text{Sm}^{2+}$ doped $\text{SrB}_4\text{O}_7$ Phosphor

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**Abstract:** Photoluminescence and color chromaticity of europium co-doped with samarium strontium-borate phosphor was studied. It was found that among the other co-dopants used, the co-doping of europium and samarium was effective in improving the luminescence and color chromaticity of  $\text{Sr}_{1-x}\text{Sm}_x\text{B}_4\text{O}_7$  at 254nm excitation. The emission spectrum of the  $\text{Sr}_{1-x}\text{Sm}_x\text{B}_4\text{O}_7$  phosphor showed peak of  $\text{Sm}^{3+}$  ions at 595 nm, and of  $\text{Sm}^{2+}$  ions at 686 nm under 254 nm excitation even after a strong reduction process.  $\text{Eu}^{2+}$  ion co-doping increased the intensity of the  $\text{Sm}^{2+}$  peak and eliminated the  $\text{Sm}^{3+}$  peak. Thus, under 254 nm excitation, the europium co-doping shifted the luminescence to a deep red region.

**Keywords:** Red Phosphor; Samarium Luminescence; Co-doping effect.

### Introduction

The major challenges in display technology today are to design a novel red phosphor that emits the light at the desired wavelength with good colour co-ordinates. Most of applications that employ oxide red phosphors have been suffering from color purity problems. For instance, plasma display panel (PDP) does not generate pure deep red color because the CIE chromaticity y value of most popularly used borate red phosphor for PDP can not reach a standard value (0.67) declared by national television standard committee (NTSC) but is still at best around 0.65. Recent experimental work has shown that  $\text{Sm}_x\text{B}_6\text{O}_{10}$ :  $\text{Sr}_{1-x}$  phosphor emits deep red colour only at 400 nm region. This is an ultraviolet emitting phosphor with a main peak at 686nm and can be excited at 254 and 400 nm. In fact,  $\text{Sm}^{2+}$  doped strontium borates or haloborates have attracted interest due to their ability to exhibit spectral hole burning [1,2]. In order to develop an efficient phosphor, various co-dopants such as Ce, Mn, Mg, Zn, Ca, and Ba are incorporated in samarium doped strontium borate. However role of europium and magnesium co-doping with samarium was only important in increasing the luminescence.

We carried out synthesis based on  $\text{Sm}_2\text{O}_3$  doped  $\text{SrO} - \text{B}_2\text{O}_3$  system by using a conventional solid-state reaction method in an attempt to achieve  $\text{Sm}^{2+}$  doped  $\text{SrB}_4\text{O}_7$  phosphors. Although applied stoichiometry of samarium doped strontium borate used here was  $\text{SrB}_6\text{O}_{10}$ :  $\text{Sm}^{2+}$  but by measuring the XRD and comparing with JCPDS card, its structure obtained was similar to samarium doped strontium tetraborate ( $\text{SrB}_4\text{O}_7$ :  $\text{Sm}^{2+}$ ). It was of our concern to eliminate trivalent samarium ions, which reside in the  $\text{SrB}_4\text{O}_7$  host even after a conventional strong reduction process by hydrogen gas flow during high temperature firing. In fact, the residual  $\text{Sm}^{3+}$  ions

deteriorate the luminescent intensity as well as color chromaticity of  $\text{Sm}^{2+}$  ions in the  $\text{SrB}_4\text{O}_7$  host. To sort out this problem,  $\text{Eu}^{2+}$  co-doping was adopted so that we could achieve the complete reduction from  $\text{Sm}^{3+}$  to  $\text{Sm}^{2+}$ .

### Experimental

The polycrystalline  $\text{SrB}_4\text{O}_7$ :  $\text{Sm}^{2+}$ ,  $\text{Eu}^{2+}$  materials were prepared by a solid-state reaction using stoichiometric quantities of high purity oxides: Strontium oxide ( $\text{SrO}$ , Sigma Aldrich, 99.99%), Orthoboric acid ( $\text{H}_3\text{BO}_3$ , Sigma Aldrich, 99.99%), Samarium oxide ( $\text{Sm}_2\text{O}_3$ , Sigma Aldrich, 99.99%) and Europium oxide ( $\text{Eu}_2\text{O}_3$ , Sigma Aldrich, 99.99%). The stoichiometric mixture (with respect to the cation stoichiometry) was mixed by dry grinding using an agate mortar and pestle, placed in a quartz boat at first preheated in air at 600 °C for 1 h then again grounded and heated at 800 °C for another 1 h in the presence of nitrogen. The resulting products were again grounded and fired for 3 h at 900 °C under a reducing atmosphere of 5% $\text{H}_2$ -95%  $\text{N}_2$  stream in a horizontal tube furnace. The  $\text{SrO}/\text{B}_2\text{O}_3$  ratio was varied from 1/2 to 1/3 and the samarium concentration was varied from 0.005 to 0.12 mol.

The phase analysis of all obtained powder samples were carried out by powder X-ray diffraction (XRD). No impurity phases were detected in the XRD patterns. The emission and excitation spectra of different samples at room temperature were determined with Perkin-Elmer LS-55 spectrophotometer equipped with a Xenon flash lamp. All the measurements were carried out under the excitation of 254 nm and with the delay and gate time fixed at 10  $\mu\text{s}$  and 5 ms, respectively. Continuous wave (CW) spectra of  $\text{SrB}_4\text{O}_7$ :  $\text{Sm}^{2+}$ ,  $\text{Eu}^{2+}$  and  $\text{SrB}_4\text{O}_7$ :  $\text{Sm}^{2+}$  were also recorded at room temperature.

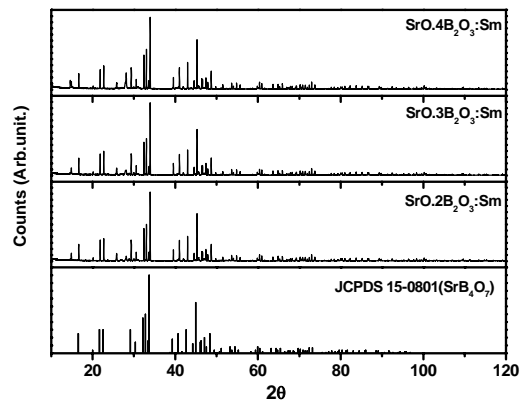
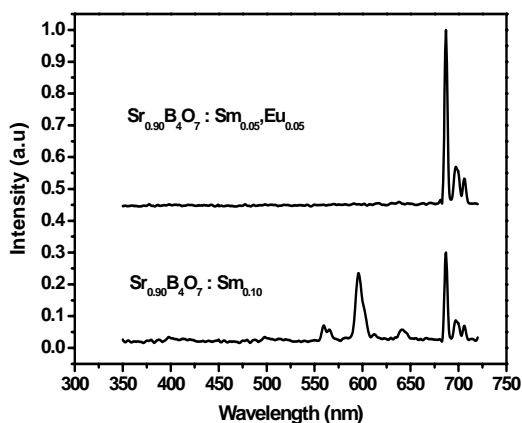


Figure1. XRD patterns

## Results and Discussion

The XRD pattern is shown in Fig.1, which showed the different host optimization stoichiometry in SrO-B<sub>2</sub>O<sub>3</sub>, such as 1/2, 1/3, 1/4. Among these stoichiometries, only SrO-3B<sub>2</sub>O<sub>3</sub> was able to give the best intensity, so this stoichiometry was chosen for further experiments. Though the applied stoichiometry of Samarium strontium borates was Sm<sub>x</sub>B<sub>6</sub>O<sub>10</sub>: Sr<sub>1-x</sub> but comparing with JCPDS card, its structure obtained was similar to samarium doped strontium tetraborate (SrB<sub>4</sub>O<sub>7</sub>: Sm<sup>2+</sup>). This compound was crystallized in an orthorhombic structure with space group P2<sub>1</sub>nm (31) and lattice parameters: a = 4.237(1) Å, b = 4.431(4) Å, c = 10.706(4) Å.

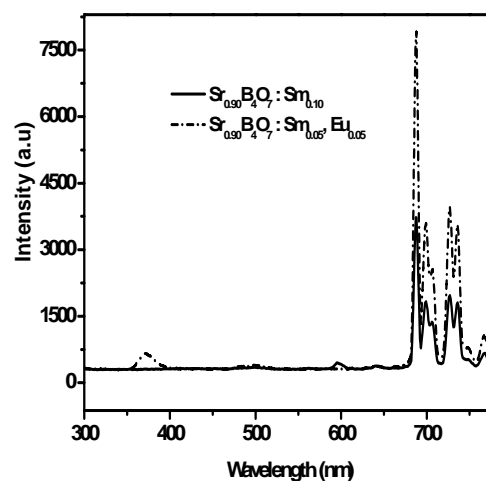


**Figure 2.** Emission spectrum of SrB<sub>4</sub>O<sub>7</sub>: Sm<sup>2+</sup> and SrB<sub>4</sub>O<sub>7</sub>: Sm<sup>2+</sup>, Eu<sup>2+</sup> under 254nm excitation.

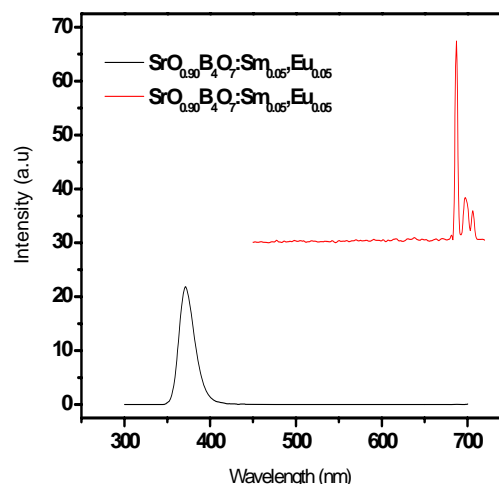
Fig.2. shows the emission spectrum of SrB<sub>4</sub>O<sub>7</sub>: Sm<sup>2+</sup>, and SrB<sub>4</sub>O<sub>7</sub>: Sm<sup>2+</sup>, Eu<sup>2+</sup> wherein emission peaks from both Sm<sup>2+</sup> and Sm<sup>3+</sup> can clearly be seen in the former while Sm<sup>3+</sup> transition was completely disappeared in the latter. The transitions of Sm<sup>3+</sup> ions in of SrB<sub>4</sub>O<sub>7</sub>: Sm<sup>2+</sup> shows the three groups of sharp emission lines located at 560, 595 and 642 nm [3]. Among the measured emission transitions of Sm<sup>3+</sup> the most significant transition is due to <sup>4</sup>G<sub>5/2</sub> → <sup>6</sup>H<sub>7/2</sub>, showing a prominent luminescence band at 595 nm. The appearance of a prominent peak at 686 nm was due to the reduction of Sm<sup>2+</sup> ions. The high intensity and sharpness of this peak is due to an intra-4f <sup>5</sup>D<sub>0</sub> → <sup>7</sup>F<sub>0</sub> transition.

As a result of europium co-doping along with samarium, complete reduction was accomplished and the intensity of the Sm<sup>2+</sup> luminescence was enhanced at 254 nm excitation. To confirm the disappearance of the Sm<sup>3+</sup> emission peaks, another PL measurement of an emission spectrum under continuous wave (CW) excitation was carried out, so that the overall emission spectrum in a wider range of wavelength from 300 to 750 nm, covering the entire visible range, was obtained, as can be seen in Fig. 3. Previously an attempt was made to prove the presence of Sm<sup>2+</sup> transition by the laser excited high-resolution luminescence [4]. The presence of both the Eu and Sm in strontium borate can be seen through CW

spectra shown in Fig.3.

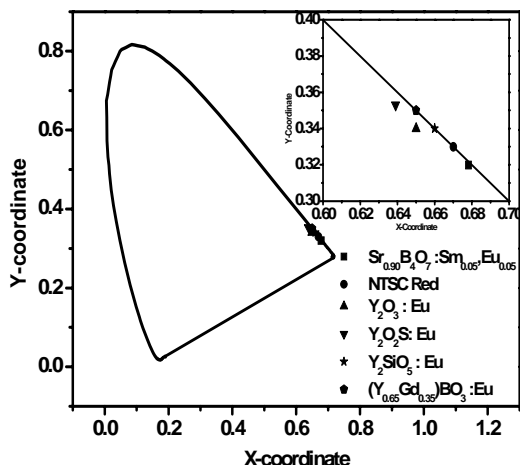


**Figure 3.** Emission spectrum of SrB<sub>4</sub>O<sub>7</sub>: Sm<sup>2+</sup>, Eu<sup>2+</sup> measured under continuous wave (CT) excitation in a wider range of wavelength.



**Figure 4.** Fluorescence spectra (black line) and Phosphorescence spectra (red line) of Sr<sub>0.90</sub>B<sub>4</sub>O<sub>7</sub>: Sm<sub>0.05</sub>, Eu<sub>0.05</sub> at 254nm excitation.

Fig.4 shows the fluorescence measurement of Eu<sup>2+</sup> at 370 nm while in phosphorescence mode (delay time = 0.5 msec, gate time= 1msec) only sharp long peak of Sm<sup>2+</sup> at 686 nm was present and Sm<sup>3+</sup> transition completely disappear. In this condition sample becomes more deep red by eliminating orange color emission from Sm<sup>3+</sup>. The allowed nature of the 4f-5d transitions [5] made the Eu<sup>2+</sup> emission decays relatively fast. The decay time is known to be typically several μsec, which is faster than the delay time adopted in the pulsed excitation mode. Therefore Eu<sup>2+</sup> emission at 370 nm was not able to detect in Fig. 2.



**Figure 5.** Colour chromaticity of  $\text{SrB}_4\text{O}_7: \text{Sm}^{2+}, \text{Eu}^{2+}$

This CW excited emission spectrum was used to calculate the CIE color chromaticity and the result ( $x = 0.67$  and  $y = 0.31$ ) shown in Fig.5. Due to the reduction of  $\text{Sm}^{3+}$  into  $\text{Sm}^{2+}$  at 254 nm excitation sample becomes more deep red by eliminating orange color emission from  $\text{Sm}^{3+}$ .

Several other co-dopants such as Ce, Mn, Mg, Zn, Ca, Ba, in addition to  $\text{Eu}^{2+}$  were also introduced in host as well as activator substitution in an attempt to enhance  $\text{Sm}^{2+}$  emission under 254 nm excitation. When Mg and Zn were introduced in the host part of  $\text{SrB}_4\text{O}_7: \text{Sm}^{2+}$  system, there was the increased in intensity of  $\text{Sm}^{3+}$  transition along with  $\text{Sm}^{2+}$  transition. Now in further experimentation the doping of Mg substituting for the Sr host and of Eu for the Sm again increased the luminescence intensity due the complete reduction of  $\text{Sm}^{2+}$  ions. By this we can deduce that role of europium

was not only important in increasing the luminous intensity at 254 nm but also in colour realization at deep red level.

## Conclusion

Effect of co-doping was the main feature in samarium doped strontium borate phosphor. The main purpose of co-doping was to increase the luminous intensity of this phosphor along with colour chromaticity at 254 nm excitation. Among various co-dopants used only europium was successful in enhancing the luminous intensity and colour chromaticity at deep red region.  $\text{Eu}^{2+}$  co-doped  $\text{Sm}^{2+}$  activated  $\text{SrB}_4\text{O}_7$  was synthesized by solid-state method and the results were characterized by XRD as well as by luminescence and continuous wave spectroscopy. Europium co-doping permits the complete reduction of  $\text{Sm}^{3+}$  ion into  $\text{Sm}^{2+}$  such that  $\text{Sm}^{3+}$  transition at 595 nm under 254 nm excitation completely disappears. Whilst most of co-doping candidates had a negligible or deteriorating influence on  $\text{Sm}^{2+}$  luminescence, only  $\text{Eu}^{2+}$  co-doping had a positive impact.

## References

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