

## Combustion Synthesis & Energy Transfer Mechanism of $\text{Bi}^{3+} \rightarrow \text{Gd}^{3+}$ in $\text{YCaBO}_4$ Phosphor

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**ABSTRACT:**  $\text{YCaBO}_4:\text{Gd}^{3+}$ , and  $\text{YCaBO}_4:\text{Gd}^{3+}, \text{Bi}^{3+}$  phosphors were synthesized by the combustion synthesis method. Photoluminescence properties of these phosphors were systematically investigated. Both the samples show the characteristic narrow band UVB emission of  $\text{Gd}^{3+}$  ions ( ${}^6\text{P}_1 \rightarrow {}^8\text{S}_{7/2}$ ). The energy transfer mechanism was studied using  $\text{Bi}^{3+}$  as sensitizer and it is observed that energy was effectively transferred to  $\text{Gd}^{3+}$ . The stoke shifts of  $\text{YCaBO}_4:\text{Gd}^{3+}$ , and  $\text{YCaBO}_4:\text{Gd}^{3+}, \text{Bi}^{3+}$  phosphors were calculated to be  $15120 \text{ cm}^{-1}$  and  $6410 \text{ cm}^{-1}$ , respectively.

**Keywords:** Combustion Synthesis, Inorganic Borate, Luminescence, Energy transfer mechanism.

**INTRODUCTION:** Ultraviolet radiation (UVR) makes up a fraction of the electromagnetic spectrum, which can be further subdivided into: UVC- the rays that do not pass through the earth's atmosphere (200-290 nm), UVB- the rays responsible for nearly all biological effects following sunlight exposure including tanning, burning and skin cancer, (290-320 nm) and UVA- those rays closest to the visible spectrum that pass through glass, and are the least harmful to the skin (320-400 nm) [1].

The use of UV radiation for phototherapy is well established. UV therapy is useful for treating more than 40 types of skin diseases and disorders [2]. When action spectra for phototherapy of psoriasis were studied [3, 4], it was found that the light belonging to longer wavelengths of UVB region was more effective while the shorter wavelengths were much less effective or even harmful. A narrow UVB source emitting at about 311 nm was made available around 1988 (van Weelden et al., 1988). This has revolutionized the UVB phototherapy [5].  $\text{LaB}_3\text{O}_6:\text{Gd}, \text{Bi}$  is a phosphor used in commercial narrow UVB phototherapy lamps. Host lattices which are easily synthesizable and structurally viable for doping at multiple cationic sites present in the lattice are of recent interest. The borate atom has two types of hybridized orbitals, the planar  $\text{sp}^2$  and the three dimensional  $\text{sp}^3$ , to coordinate three or four oxygen atoms to form various  $\text{BxO}_y$  complex anionic groups. Therefore many types of borate crystals have been found to be constructed based on these complex anionic groups. Therefore, inorganic [6] bo-

rates have long been a focus of research. Inorganic borates are excellent host materials because of their variety of structure type, large electronic band gap, transparency to a wide range of wavelengths, high optical damage threshold and high optical quality [7,8,9,10].

In this work we report the combustion synthesis of  $\text{YCaBO}_4:\text{Gd}^{3+}$ , and  $\text{YCaBO}_4:\text{Gd}^{3+}, \text{Bi}^{3+}$  and the energy transfer mechanism of  $\text{Bi}^{3+} \rightarrow \text{Gd}^{3+}$  in  $\text{YCaBO}_4$ .

**MATERIALS AND METHODS:** Borate phosphors  $\text{YCaBO}_4:\text{Gd}^{3+}$  and  $\text{YCaBO}_4:\text{Gd}^{3+}, \text{Bi}^{3+}$  were prepared by a method described in our earlier work [11,12,13]. Heat generated in the exothermic reaction between ammonium nitrate and urea is used to carry out the synthesis. Table 1 gives the details of the ingredients used in synthesis of phosphors.

**Table 1: Estimated Distance (cm) for Letter and Digit Stimuli.**

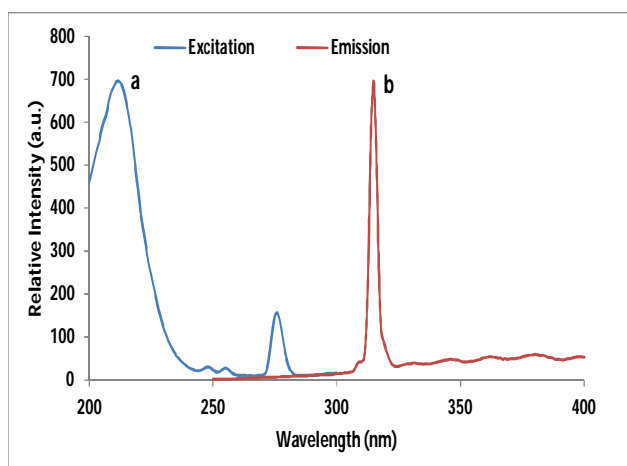
S. N.	Compound	Molar ratio
1.	$\text{Y}_{(0.97)}\text{Gd}_{0.03}\text{CaBO}_4$	$\text{Y}(\text{NO}_3)_3:\text{Ca}(\text{NO}_3)_2:\text{Gd}(\text{NO}_3)_3:\text{H}_3\text{BO}_3:\text{CO}(\text{NH}_2)_2:\text{NH}_4\text{NO}_3$ (0.97) : 1 : 0.03 : 1 : 4 : 4.5
2.	$\text{Y}_{(0.94)}\text{Gd}_{0.03}\text{Bi}_{0.03}\text{CaBO}_4$	$\text{Y}(\text{NO}_3)_3:\text{Ca}(\text{NO}_3)_2:\text{Gd}(\text{NO}_3)_3:\text{Bi}(\text{NO}_3)_3:\text{H}_3\text{BO}_3:\text{CO}(\text{NH}_2)_2:\text{NH}_4\text{NO}_3$ (0.94) : 1 : 0.03 : 0.03 : 4 : 4 : 4.5

Following the combustion, the resulting fine powders were annealed for 4 h at temperature  $800^\circ\text{C}$  and then rapidly cooled to room temperature. PL measurements at room temperature were performed on Hitachi F-

7000 Fluorescence Spectrophotometer in the range 200–500 nm. For confirmation of compound formation, X-ray diffraction patterns of all synthesized materials were recorded on Rigaku Miniflex X-ray Diffractometer and compared with the ICDD file.

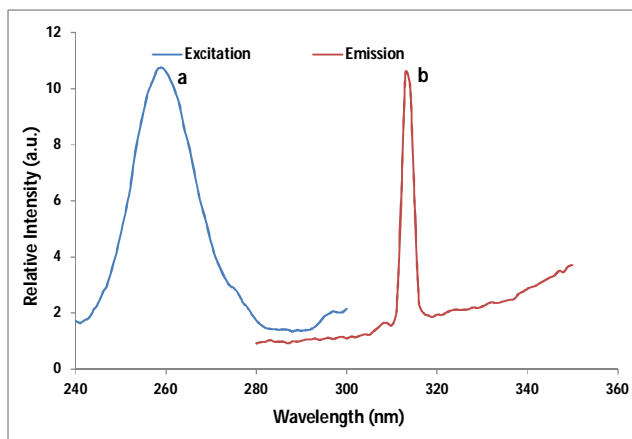
**RESULTS AND DISCUSSION:** The photoluminescence (PL) & photoluminescence excitation (PLE) measurements of all the synthesized materials were performed on Hitachi F-7000 Spectrofluorometer at room temperature with spectral slit width 2.5 nm (for both emission and excitation measurements) and PMT voltage 400 V.

Figure 1 represents the room temperature PL spectra for samples of composition Y<sub>(0.97)</sub>Gd<sub>0.03</sub>CaBO<sub>4</sub>. The emission is in form of a narrow band round 312 nm corresponding to <sup>6</sup>P<sub>J</sub> → <sup>8</sup>S<sub>7/2</sub> transition upon excitation with 276 nm. The emission spectra consists of a weak line at 304 nm followed by a strong one at 312 nm. These lines correspond to the <sup>6</sup>P<sub>5/2</sub> → <sup>8</sup>S and <sup>6</sup>P<sub>7/2</sub> → <sup>8</sup>S transitions of the Gd<sup>3+</sup> ion, respectively. The stoke shift was calculated to be 15120 cm<sup>-1</sup>.



**Figure 1:** PL spectra of Y<sub>(0.97)</sub>Gd<sub>0.03</sub>CaBO<sub>4</sub> (a)Excitation spectra monitored at 312 nm emission, & (b)Emission spectra monitored at 276 nm excitation.

Figure 2 represents the PL spectra of Y<sub>(0.94)</sub>Gd<sub>0.03</sub>Bi<sub>0.03</sub>CaBO<sub>4</sub>. The emission is in form of a narrow band round 312 nm corresponding to <sup>6</sup>P<sub>7/2</sub> → <sup>8</sup>S<sub>7/2</sub> transition upon excitation with 260 nm. The broad excitation spectrum has a maximum located at 260 nm corresponds to <sup>1</sup>S<sub>0</sub> → <sup>3</sup>P<sub>1</sub> transition of Bi<sup>3+</sup> ions. The excitation spectra show very good overlap with the Hg 253.7 nm line. The efficient energy transfer from Bi<sup>3+</sup> to Gd<sup>3+</sup> is observed. Finally the stoke shift was calculated to be 6410 cm<sup>-1</sup>.



**Figure 2:** PL spectra of Y<sub>(0.94)</sub>Gd<sub>0.03</sub>Bi<sub>0.03</sub>CaBO<sub>4</sub>. (a)Excitation spectra monitored at 312 nm emission, & (b) Emission spectra monitored at 260 nm excitation.

**CONCLUSION:** Borate phosphors were prepared by a solution combustion synthesis method followed by heating of the precursor combustion ash at 800°C for 4 h in air. The synthesized materials were characterized using powder XRD. The photoluminescent properties of Y<sub>(0.97)</sub>Gd<sub>0.03</sub>CaBO<sub>4</sub> and Y<sub>(0.94)</sub>Gd<sub>0.03</sub>Bi<sub>0.03</sub>CaBO<sub>4</sub> phosphors were investigated at room temperature. In all synthesized phosphors emission is in form of a narrow band round 312 nm corresponding to <sup>6</sup>P<sub>J</sub> → <sup>8</sup>S<sub>7/2</sub> transition. The emission spectra consists of a weak line at 304 nm followed by a strong one at 312 nm, which are corresponds to the <sup>6</sup>P<sub>5/2</sub> → <sup>8</sup>S<sub>7/2</sub> and <sup>6</sup>P<sub>7/2</sub> → <sup>8</sup>S<sub>7/2</sub> transitions of the Gd<sup>3+</sup> ion, respectively. The excitation spectra for Y<sub>(0.97)</sub>Gd<sub>0.03</sub>CaBO<sub>4</sub> and Y<sub>(0.94)</sub>Gd<sub>0.03</sub>Bi<sub>0.03</sub>CaBO<sub>4</sub> show very good overlap with the Hg 253.7 nm line. The stoke shifts of Y<sub>(0.97)</sub>Gd<sub>0.03</sub>CaBO<sub>4</sub> and Y<sub>(0.94)</sub>Gd<sub>0.03</sub>Bi<sub>0.03</sub>CaBO<sub>4</sub> phosphors were calculated to be 15120 cm<sup>-1</sup> and 6410 cm<sup>-1</sup>, respectively.

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