

# Synthesis and Photoluminescence of $\text{Eu}^{3+}$ -activated $\text{Ca}_3\text{La}_2(\text{BO}_3)_4$ Phosphor

Mudavat Srinivas

**Abstract**— Polycrystalline  $\text{Ca}_3\text{La}_2(\text{BO}_3)_4$  phosphor doped with rare-earth ions ( $\text{Eu}^{3+}$ ) were prepared by conventional solid state reaction method and the samples were sintered at  $1200^\circ\text{C}$  for 8 hours in air atmosphere. The structural characterisation was carried out by X-ray diffraction method (XRD). The Photoluminescence (PL) spectra investigated. The PL spectra indicate that the main emission peak at 611 nm under UV excitation due to  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$  transition of  $\text{Eu}^{3+}$  ions. PL peak intensity was found to increase with increase in the dopant concentration. These phosphors may provide a new kind of luminescent material for light emitting diodes under uv excitation.

**Index Terms**— Optical materials, Chemical synthesis, X-ray diffraction, Luminescence

## I. INTRODUCTION

In recent years, a great amount of interest in phosphors has been brought into rapid developments in the promising display and illumination technologies such as plasma display panels (PDPs), light emitting diodes (LEDs), field emission displays (FEDs), and electroluminescence displays (ELDs) [1-3]. Among these displays the attention of many researchers made on light emitting diodes and it has begun replacing conventional lighting sources due to its advantages such as low power consumption, high brightness, longer working performance, high energy efficiency and low environmental effect. The fabrication of white-LEDs involves a blue-emitting InGaN chip and  $\text{Y}_3\text{Al}_5\text{O}_{12}:\text{Ce}^{3+}$  phosphor is emitting yellow emission [4-10], this combination displays have low color rendering indices (CRIs) and high color temperature is due to the insufficiency of red emission in the visible light spectrum [8].

Thus, it is very essential to search for new red light can be used effectively to compensate for the red emission deficiency of the LED output light. For general lighting, photoluminescent materials including oxides, silicates, aluminates, aluminoborates, aluminosilicates, nitrides, borates etc., play very important for the potential applications in ultraviolet devices. For example the ultraviolet light emitting diodes (UVLED) is necessary to combine a UV chip with red, green and blue (RGB) phosphor to generate white lights. Among these host investigated, borates are good candidates as host structure due to their chemical stable, low synthetic temperature, easy preparation and high luminescent brightness [11]. The luminescence properties of UV-excitable  $\text{Eu}^{2+}$  doped borate phosphors such as  $\text{Ba}_2\text{Ca}(\text{BO}_3)_2$ ,  $\text{Sr}_2\text{Mg}(\text{BO}_3)_2$ ,  $\text{Ba}_2\text{Mg}(\text{BO}_3)_2$ ,  $\text{Ba}_2\text{LiB}_5\text{O}_{10}$  and  $\text{SrAl}_2\text{B}_2\text{O}_7$

have been reported in the literatures [12-16]. Apart from  $\text{Eu}^{2+}$ -activated borates, several  $\text{RE}^{3+}$ -doped borates have also been studied, such as  $\text{BaAl}_2\text{B}_2\text{O}_7$ ,  $(\text{Y,Gd})\text{BO}_3$ ,  $\text{BaB}_8\text{O}_{13}$ ,  $\text{CaAl}_2\text{B}_2\text{O}_7$ ,  $\text{CaYBO}_4$ , and  $\text{Sr}_3\text{Y}_2(\text{BO}_3)_4$  [17- 24]. In this paper we report the  $\text{Ca}_3\text{La}_2(\text{BO}_3)_4$  phosphor regarded as a potential as host material owing to its excellent chemical, physical and optical properties [25,26].

## II. MATERIALS AND METHODS

The Phosphor materials of composition  $\text{Ca}_3\text{La}_2(\text{BO}_3)_4$  [CLB] doped with europium were synthesized by the conventional solid state reaction method. Stoichiometric amounts of AR grade  $\text{CaCO}_3$ ,  $\text{La}_2\text{O}_3$ ,  $\text{Eu}_2\text{O}_3$  and  $\text{H}_3\text{BO}_3$  were thoroughly mixed and ground together with ethanol in an agate mortar for 5 hours to give homogenous mixture. The resultant powders were initially dried at  $100^\circ\text{C}$  for 1 h, kept in an alumina boat and heated at  $1200^\circ\text{C}$  in air for 8 hrs. Later, the temperature is brought down to  $950^\circ\text{C}$  and the samples were held at that temperature for 1 hour in air. These samples were rapidly cooled down to room temperature and were grinded to get fine powder for further studies.

The phase purity of the as synthesized phosphor were characterized using X-ray diffraction (XRD) patterns with  $\text{Cu-K}\alpha$  radiation of wave length  $1.5406 \text{ \AA}$  in the  $2\theta$  range of  $10 \sim 80^\circ$  with a step size of  $0.04^\circ/\text{sec}$ . The operation voltage and current of the instrument were maintained at 40 kV and 30 mA respectively.

The compositions of the phosphor samples were obtained from energy dispersive spectrum (EDS). The EDS was attached to the HITACHI S-3700N model instrument. The photoluminescence spectra were measured using Spectrofluorophotometer (Shimadzu, RF 5301 PC) with a 150 w a xenon arc lamp. All measurements were recorded at room temperature.

## III. RESULT AND DISCUSSIONS

### 3.1. Powder XRD

The powder X-ray diffractograms of CLB are shown in fig.1 and the observed d-lines are indexed for higher concentration of  $\text{Eu}^{3+}$  shown in fig.2. The CLB belongs to the orthorhombic system with space group  $Pnam$ , and unit cell parameters are show as following:  $a = 7.279 \text{ \AA}$ ,  $b = 16.417 \text{ \AA}$ ,  $c = 8.654 \text{ \AA}$ . All the compounds are very close to that of reported values for CLB [27]. It is indicated that the doping  $\text{Eu}^{3+}$  ions do not form new phases in the synthesis process.

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Mudavat Srinivas, Department of Physics, University College of Science, Osmania University, Hyderabad, India

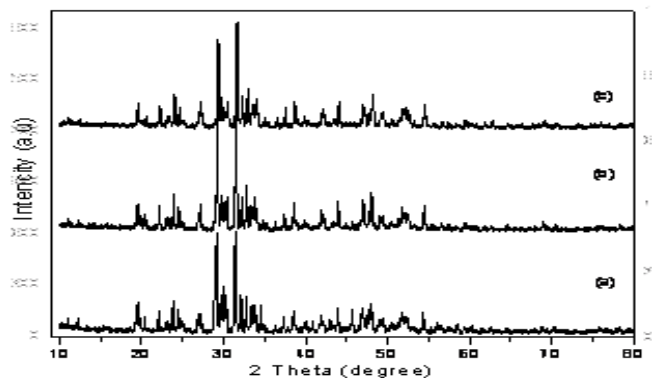


Figure 1 XRD patterns of  
 (a) Ca<sub>3</sub>La<sub>1.98</sub>Eu<sub>0.02</sub>(BO<sub>3</sub>)<sub>4</sub>  
 (b) Ca<sub>3</sub>La<sub>1.94</sub>Eu<sub>0.06</sub>(BO<sub>3</sub>)<sub>4</sub>  
 (c) Ca<sub>3</sub>La<sub>1.90</sub>Eu<sub>0.1</sub>(BO<sub>3</sub>)<sub>4</sub> phosphors

The structure of CLB is formed by isolated BO<sub>3</sub> triangles, calcium-oxygen polyhedral, and lanthanum-oxygen polyhedral. The trivalent lanthanum ions occupy two different crystallographic sites (La<sub>1</sub> and La<sub>2</sub>), and every La<sup>3+</sup> has an eight-fold coordination to form LaO<sub>8</sub> polyhedra. The bond valence of La<sub>1</sub> is stronger than that of La<sub>2</sub>, so Eu<sup>3+</sup> prefers to occupy the La<sub>2</sub> site. La<sub>2</sub>O<sub>8</sub> polyhedra columns are built by sharing edges along the c-axis. The distance between La<sub>1</sub> and La<sub>2</sub> is equal to the value of the c-constant, and the environment around La<sup>3+</sup> is not centrosymmetric. The structure of CLB indicate that the long distance between the rare-earth ions could result in a higher doping concentration, and the imperfection symmetry of Eu<sup>3+</sup> will introduce of the pure emission.

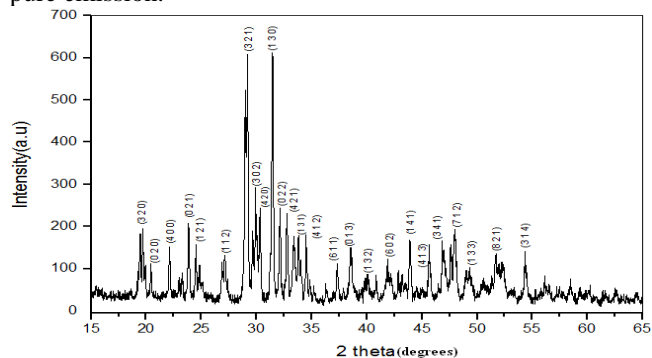
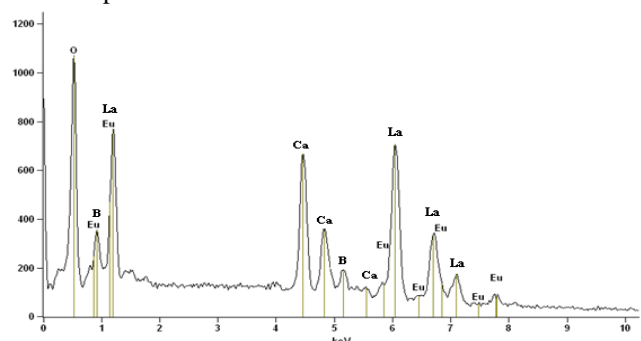


Figure 2 XRD pattern of Ca<sub>3</sub>La<sub>1.9</sub>Eu<sub>0.1</sub>(BO<sub>3</sub>)<sub>4</sub> phosphor

### 3.2. Energy Dispersive Spectrum

The energy dispersive spectrum analysis of 0.1 mol % Eu<sup>3+</sup> doped CLB sample peaks shown in Fig.3 corresponding to Ca, La, Eu, B and O. The EDS pattern confirms the presence of europium in the CLB powders and its wt% is nearly equal to the doped value of Eu in CLB.



#### 3.3.1 The Spectroscopic properties of Ca<sub>3</sub>La<sub>2</sub>(BO<sub>3</sub>)<sub>4</sub>: Eu<sup>3+</sup>

The spectroscopic properties of Eu<sup>3+</sup> activated Ca<sub>3</sub>La<sub>2</sub>(BO<sub>3</sub>)<sub>4</sub> phosphor which can efficiently emit under UV light excitation and the excitation spectrum of CLB is shown in fig.3.

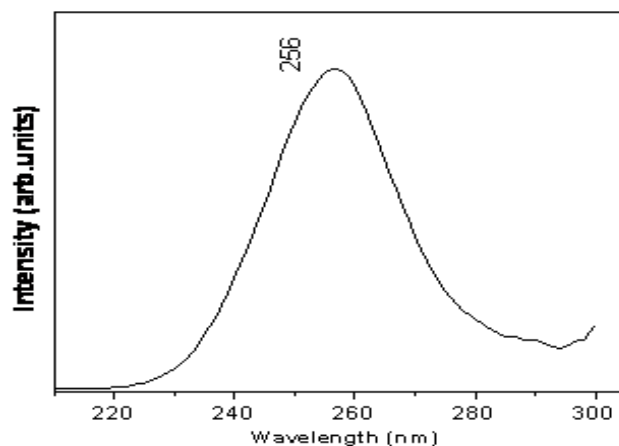


Fig.3 Excitation spectrum of CLB for 0.1 Eu<sup>3+</sup> concentration

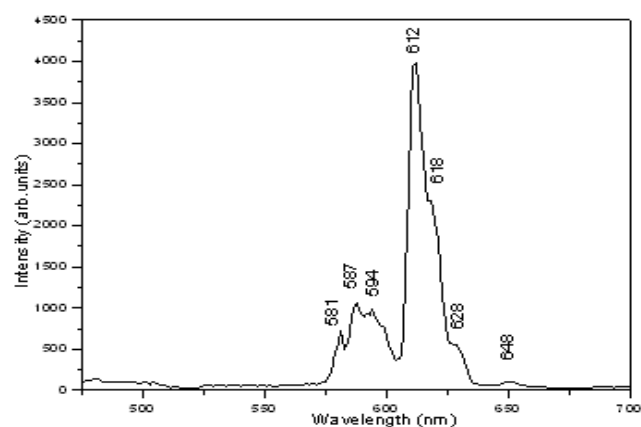


Fig.4 Emission spectrum of CLB phosphor for 0.1 Eu<sup>3+</sup> concentration

The emission spectrum of CLB phosphor recorded under the 256 nm excitation shown in fig.4. It shows that several narrow bands can be observed between 580 nm and 700 nm. The main emission is observed at 612 nm, which is due to the electric dipole transition of <sup>5</sup>D<sub>0</sub>→<sup>7</sup>F<sub>2</sub> of Eu<sup>3+</sup>. This is because the Eu<sup>3+</sup> occupies the non-centrosymmetric position in the crystal structure of Ca<sub>3</sub>La<sub>2</sub>(BO<sub>3</sub>)<sub>4</sub>. Other emissions are corresponding to transition of <sup>5</sup>D<sub>0</sub>→<sup>7</sup>F<sub>j</sub> (j=1,2,3) such as the emissions at 594 nm, 628 nm and 648 nm due to the <sup>5</sup>D<sub>0</sub>→<sup>7</sup>F<sub>1</sub>, <sup>5</sup>D<sub>0</sub>→<sup>7</sup>F<sub>2</sub>, <sup>5</sup>D<sub>0</sub>→<sup>7</sup>F<sub>3</sub> transitions of Eu<sup>3+</sup> respectively. Eu<sup>3+</sup> rare earth ions are a well known candidate in obtaining a red-emitting due to its lowest excited level <sup>5</sup>D<sub>0</sub> of the 4f<sup>6</sup> configuration which is located below the 4f<sup>6</sup>5d configuration and it displays very sharp red emission lines at <sup>5</sup>D<sub>0</sub>→<sup>7</sup>F<sub>2</sub> due to electrical dipole transition around 611 ~ 617 nm [28,29].

### 4.0 Conclusions

Ca<sub>3</sub>La<sub>2</sub>(BO<sub>3</sub>)<sub>4</sub> were synthesized by conventional high temperature solid state reaction method and Single-phased phosphors have attracted much attention in the fabrication of white LED. The PL spectra indicate that the main emission peak at 612 nm under UV excitation due to <sup>5</sup>D<sub>0</sub>→<sup>7</sup>F<sub>2</sub> transition of Eu<sup>3+</sup> ions. PL peak intensity was found to increase with increase in the dopant concentration. These phosphors may provide a new kind of luminescent material for light emitting diodes under ultraviolet excitation.

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