



**STRUCTURAL AND LUMINESCENCE PROPERTIES OF Sm<sup>3+</sup>/Eu<sup>3+</sup> CO-DOPED 2CaO-B<sub>2</sub>O<sub>3</sub>-P<sub>2</sub>O<sub>5</sub> PHOSPHORS: ENERGY TRANSFER MECHANISM AND ENHANCEMENT OF RED LUMINESCENCE BY TEMPERATURE**

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**ABSTRACT**

Sm<sup>3+</sup>/Eu<sup>3+</sup> co-doped calcium borophosphate phosphors were synthesized by solid state reaction method. 2CaO-B<sub>2</sub>O<sub>3</sub>-P<sub>2</sub>O<sub>5</sub>: Sm<sup>3+</sup>/Eu<sup>3+</sup> co-doped phosphors were characterized by XRD, SEM, DRS, FT-IR, <sup>31</sup>P solid state NMR, excitation, photoluminescence (PL) and decay profiles. XRD profiles showed that the prepared phosphors exhibit a hexagonal phase in crystal structure and SEM results showed that the particles are more irregular morphologies. FT-IR spectrum shows prominent band at 1029 cm<sup>-1</sup> which is due to the asymmetric stretching vibrations of [PO<sub>4</sub>]<sup>3-</sup> tetrahedrons. From <sup>31</sup>P NMR spectra of Sm<sup>3+</sup>/Eu<sup>3+</sup> co-doped 2CaO-B<sub>2</sub>O<sub>3</sub>-P<sub>2</sub>O<sub>5</sub> (CBP) phosphors, it was observed that the chemical shifts are located in the positive frequency region indicating the presence of mono-phosphate complexes Q<sup>0</sup>-(PO<sub>4</sub><sup>3-</sup>). Photoluminescence spectra of Sm<sup>3+</sup>/Eu<sup>3+</sup> co-doped CBP phosphors show increase in emission intensity of Eu<sup>3+</sup> ion due to co-doping with Sm<sup>3+</sup> ions due to energy transfer process. The energy transfer mechanism between Sm<sup>3+</sup> and Eu<sup>3+</sup> ions has been clearly explained. The energy transfer process has been evidenced by lifetime decay profiles. From CIE chromaticity diagram, pure red color emission was observed in 0.6Sm<sup>3+</sup>/0.6Eu<sup>3+</sup> co-doped CBP phosphors. These results suggest that the prepared phosphors are potential for red luminescent optical materials.

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**INTRODUCTION**

Currently, great interest in phosphors has resulted in rapid developments in the solid state lighting sources, including LED display and illumination technologies. The applications of white light from combined blue emission of blue chip and yellow light emitted by YAG:Ce<sup>3+</sup> have been limited in many fields due to the lack of red light harmonic [1, 2]. Thus, the lack of red phosphors for long term constitutes a serious obstacle to the development of advanced LED-based technologies. Therefore, one way of developing practical white LEDs is to search for both high efficiency and quality red phosphors to improve color rendering [3]. A series of red phosphors have been investigated using the compounds such as nitrides, silicates, sulfides, and molybdates et al. [4, 5].

Rare earth (RE) ion doped phosphors have considerable attention for diverse applications such as solid state lasers, waveguides and optical fibers. RE ions have 4f-4f and 4f-5d electronic transitions, which exhibit sharp emission lines from the ultraviolet (UV) to the infrared (NIR) regions [6]. Among RE ions, Eu<sup>3+</sup> has good energy level structure and high luminescence efficiency of <sup>5</sup>D<sub>0</sub>→<sup>7</sup>F<sub>2</sub> transition, which is very sensitive to changes in chemical surroundings of the Eu<sup>3+</sup> ion. On the other hand for Sm<sup>3+</sup> ion, the ionic radius is nearly

same compared to Eu<sup>3+</sup>, gives a red color emission, sometimes shifted to longer wavelengths compared to Eu<sup>3+</sup> [7]. It's emitting level; <sup>4</sup>G<sub>5/2</sub> gives relatively high quantum efficiency and also shows different emission quenching [8].

The energy transfer between two RE ions co-doped in phosphors has been studied in many systems. The reason is that the sensitized luminescence is not only of interest for applications but also for understanding the basic mechanisms involved [9-11]. In Sm<sup>3+</sup> and Eu<sup>3+</sup> co-doped phosphors, the excitation wavelength range of Eu<sup>3+</sup> emission is broadened owing to the energy transfer from Sm<sup>3+</sup> to Eu<sup>3+</sup> [12]. Many researchers have discussed the phenomena of radiative and non-radiative transitions in Sm<sup>3+</sup>/Eu<sup>3+</sup> co-doped phosphors and succeeded in realizing energy transfer in co-doped phosphors. Matwa et al. studied photoluminescence and energy transfer of Eu<sup>3+</sup> and Sm<sup>3+</sup> single-doped and co-doped BaB<sub>8</sub>O<sub>13</sub> phosphors [13]. Hachani et al. discussed energy transfer between Sm<sup>3+</sup> and Eu<sup>3+</sup> in YPO<sub>4</sub>, LaP<sub>5</sub>O<sub>14</sub> and LaP<sub>3</sub>O<sub>9</sub> phosphates: potential quantum cutters for red emitting phosphors [14]. Wembo et al. studied luminescent properties and energy transfer mechanism of NaGd(MoO<sub>4</sub>)<sub>2</sub>:Sm<sup>3+</sup>/Eu<sup>3+</sup> phosphors [15]. Fengwen et al. reported luminescence and red long after glow investigation of Eu<sup>3+</sup>/Sm<sup>3+</sup> co-doped CaWO<sub>4</sub> phosphor [16].

CBP phosphors show significance for white LED (WLED) applications and some research work on Sm<sup>3+</sup> and Eu<sup>3+</sup> singly

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doped phosphors was done recently [17]. In the present paper, an attempt is made to report the influence of different concentrations of Sm<sup>3+</sup> ion on the Eu<sup>3+</sup> ion photoluminescence in Sm<sup>3+</sup>/Eu<sup>3+</sup> co-doped CBP phosphors. Changes in spectroscopic properties as a function of concentration were observed and discussed in terms of local environment of Sm<sup>3+</sup> and Eu<sup>3+</sup> ions. In the present work, the structural, thermal and luminescence properties of new red emitting CBP phosphor co-doped with Sm<sup>3+</sup>/Eu<sup>3+</sup> ions was reported. Eu<sup>3+</sup> has been taken as acceptor ion and Sm<sup>3+</sup> as donor ion. Surprisingly, four common excitation bands are observed in Eu<sup>3+</sup> and Sm<sup>3+</sup> consisting phosphors, with these excitations the emission performances have been observed and the energy transfer phenomenon has been explained by increasing the donor (Sm<sup>3+</sup>) concentration. The energy transfer mechanism has clearly explained between Sm<sup>3+</sup> and Eu<sup>3+</sup> ions with lifetime decay profiles.

### Experimental

Using solid state reaction method, Sm<sup>3+</sup>/Eu<sup>3+</sup> co-doped 2CaO-B<sub>2</sub>O<sub>3</sub>-P<sub>2</sub>O<sub>5</sub> (CBP) phosphors ((1.4-x)CaO-B<sub>2</sub>O<sub>3</sub>-P<sub>2</sub>O<sub>5</sub>-xSm<sub>2</sub>O<sub>3</sub>-0.6Eu<sub>2</sub>O<sub>3</sub> (where x=0.2, 0.4, 0.6, 0.8 and 1.0 mol%)) were prepared using raw materials, CaCO<sub>3</sub>, H<sub>3</sub>BO<sub>3</sub>, NH<sub>4</sub>H<sub>2</sub>PO<sub>4</sub>, Sm<sub>2</sub>O<sub>3</sub> and Eu<sub>2</sub>O<sub>3</sub> with 99.9 % purity. The batch of 10 gm was weighed as per the composition given above. These materials were taken in an agate mortar and after ground they are preheated at 650 °C for 2 h in porcelain crucible and then cooled down to room temperature. The preheated batches were again heated at 950 °C for 4 h in an electrical furnace. The obtained phosphor powders were pulverized for further characterization and analysis.

Phase purity of Sm<sup>3+</sup>/Eu<sup>3+</sup> co-doped CBP phosphors were characterized by X-ray diffraction (XRD) with Philips PW 1050 instrument, using Ni filtered Cu tube with K $\alpha$  radiation. SEM images of Sm<sup>3+</sup>/Eu<sup>3+</sup> co-doped phosphors were taken by Carl Zeiss EVO-MA15 scanning electron microscope. The UV-visible diffuse reflectance spectra (DRS) were measured for undoped and co-doped Sm<sup>3+</sup>/Eu<sup>3+</sup> phosphors using JASCO V570 UV-Vis-NIR spectrometer. The thermal decomposition of CBP phosphors was performed by thermo gravimetry differential scanning calorimetry (TG-DSC; Model NETZSCH STA 449C, Selb, Germany) in air atmosphere with a heating rate 10 °C/min. The fourier transform infrared spectra were recorded at room temperature with 4 cm<sup>-1</sup> spectral resolution between 400 and 4000 cm<sup>-1</sup> by a BRUKER FTIR spectrometer. Solid state <sup>31</sup>P NMR spectra were obtained at 400 MHz using a JOEL ECX400 DELTA2 NMR spectrometer with a 4 mm probe. Excitation, photoluminescence, decay lifetimes and quantum yield were acquired using FLS-920 Edinburg-fluorimeter (Horiba FL3-22iHR320).

## RESULTS AND DISCUSSION

### X-ray diffraction spectra (XRD)

Sm<sup>3+</sup>/Eu<sup>3+</sup> co-doped XRD patterns of CBP phosphors were measured in the range, 10°-80° and were shown in Fig. 1. By comparing the obtained XRD patterns of present co-doped phosphors with host pattern, all samples showed the same diffraction peaks reported in JCPDS card No: 0-018-0283 and are in good agreement. It was also found that, with the increase of doping concentrations, showed same JCPDS

structure, thus implying the formation of pure crystalline phase of CBP: Sm<sup>3+</sup>/Eu<sup>3+</sup> co-doped phosphors. Generally, borophosphate crystal contains CaO<sub>9</sub>, BO<sub>4</sub> and PO<sub>4</sub> polyhedron, generating three-dimensional composite frame work with large tunnels inside [18]. In CBP crystal, insertion of Sm<sup>3+</sup>/Eu<sup>3+</sup> took in the nine-fold coordinate calcium site due to similar ionic radii of Sm<sup>3+</sup>, Eu<sup>3+</sup> and Ca<sup>2+</sup> ions. Sm<sup>3+</sup>/Eu<sup>3+</sup> ions occupy a site in nine coordinated large polyhedron occurring in tortuous vertical columns formed by BO<sub>4</sub> and PO<sub>4</sub> tetrahedra [19]. A well crystallized hexagonal symmetry with group space P6cc (184) was observed from figure 1.

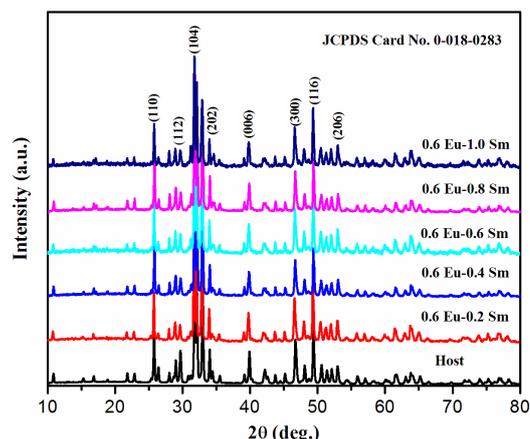


Fig 1 XRD profiles of Sm<sup>3+</sup>/Eu<sup>3+</sup> co-doped 2CaO-B<sub>2</sub>O<sub>3</sub>-P<sub>2</sub>O<sub>5</sub> phosphors.

### SEM morphology

SEM images are shown in Fig. 2 (a-e) for different concentrations of Sm<sup>3+</sup>/Eu<sup>3+</sup> co-doped CBP phosphors (a:0.2Sm/0.6Eu, b:0.4Sm/0.6Eu, c:0.6Sm/0.6Eu, d:0.8Sm/0.6Eu, e:1.0Sm/0.6Eu). From the figure, it was found that the particle size has increased as the Sm<sup>3+</sup> concentration increased from 0.2 to 1.0 mol% with 0.6 mol% of Eu<sup>3+</sup>, and the particles

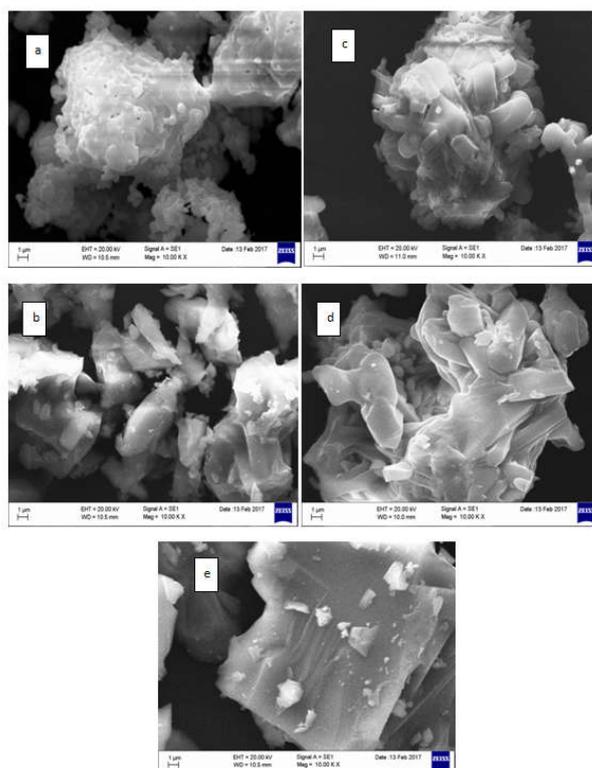


Fig 2 SEM images of Sm<sup>3+</sup>/Eu<sup>3+</sup> co-doped 2CaO-B<sub>2</sub>O<sub>3</sub>-P<sub>2</sub>O<sub>5</sub> phosphors.

have more irregular morphologies due to  $\text{Sm}^{3+}/\text{Eu}^{3+}$  incorporation. In the present work, the sizes of the particles are between few microns and several tens of microns and they are suitable for use in the WLEDs applications.

### Diffuse reflection spectra (DRS)

The diffuse reflection spectra (DRS) of  $\text{Sm}^{3+}/\text{Eu}^{3+}$  co-doped and undoped CBP phosphors in the visible range are shown in Fig. 3. From the reflection spectra it was observed that undoped and co-doped spectra have similar in shape indicating that the effect of co-doping of  $\text{Sm}^{3+}/\text{Eu}^{3+}$  ions on the reflection spectra is negligible. The band gaps were obtained from the diffuse reflection spectra of both the phosphors using the formula given in ref. [20] and these values are 4.72 eV and 4.78 eV for undoped and  $0.6\text{Sm}^{3+}/0.6\text{Eu}^{3+}$  co-doped phosphors, respectively.

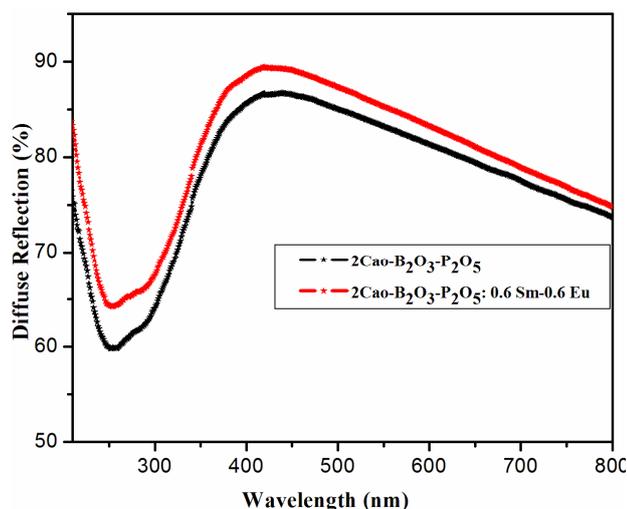


Fig 3 DRS spectra of  $2\text{CaO}\cdot\text{B}_2\text{O}_3\cdot\text{P}_2\text{O}_5$  and  $\text{Sm}^{3+}/\text{Eu}^{3+}$  co-doped  $2\text{CaO}\cdot\text{B}_2\text{O}_3\cdot\text{P}_2\text{O}_5$  phosphors.

### FT-IR spectra

Fourier transform infrared spectrum of present phosphor was measured in the range  $500\text{--}3800\text{ cm}^{-1}$  and shown in Fig. 4.

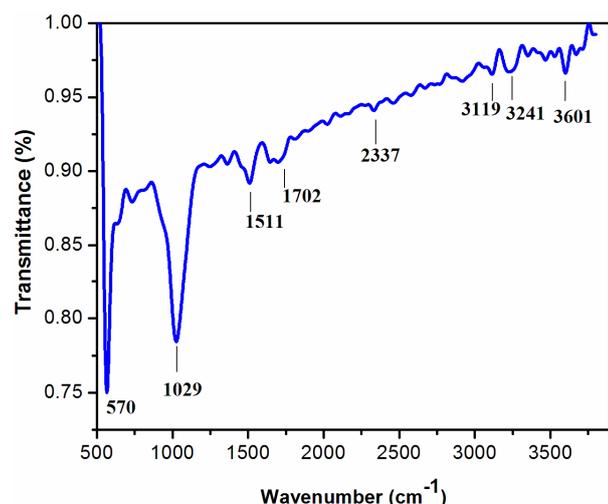


Fig 4 FT-IR spectrum of  $2\text{CaO}\cdot\text{B}_2\text{O}_3\cdot\text{P}_2\text{O}_5$  phosphor

From the figure, it is observed that the spectrum consists of eight bands centered at  $\sim 570$ ,  $\sim 1029$ ,  $\sim 1511$ ,  $\sim 1702$ ,  $\sim 2337$ ,  $\sim 3119$ ,  $\sim 3241$  and  $\sim 3601\text{ cm}^{-1}$ . The bands at  $570$ ,  $1029$  and  $1511\text{ cm}^{-1}$  are attributed to the  $(\text{PO}_4)^{3-}$  vibrational bands [21] and correspond to asymmetric stretching vibrations. The band

at  $570\text{ cm}^{-1}$  is due to O-P-O asymmetric bending vibrations, while the band at  $1029\text{ cm}^{-1}$  is due to O-P-O asymmetric stretching vibrations of  $[\text{PO}_4]^{3-}$  tetrahedrons [21]. The band at  $1511\text{ cm}^{-1}$  is attributed to the asymmetric stretching of C-O bonds [22]. The bands observed between the energy range  $1702\text{--}3601\text{ cm}^{-1}$  are assigned to the H-O-H bending vibrational mode of the  $\text{H}_2\text{O}$  molecule.

### $^{31}\text{P}$ solid state NMR spectra:

$^{31}\text{P}$  solid state NMR is one of the important tool in characterizing the structures of phosphate-type phosphors due to the chemical shifts being sensitive to the phosphorus environment. The phosphate bonding is explained through  $\text{Q}^n$  species, where the superscript  $n$  refers to the number of bridging oxygens per tetrahedron [23].  $^{31}\text{P}$  NMR spectra of CBP and  $\text{CBP}:0.6\text{Sm}^{3+}/0.6\text{Eu}^{3+}$  phosphors are shown in Fig. 5. In the present work, the obtained spectra (from Fig. 5) are a single, symmetric Gaussian peak and position of line for CBP and  $\text{CBP}:0.6\text{Sm}^{3+}/0.6\text{Eu}^{3+}$  phosphors are at  $+3.9\text{ ppm}$ . This value indicates the presence of mono-phosphate complexes  $\text{Q}^0\text{-(PO}_4^{3-})$  (phosphate tetrahedral with zero bridging oxygens) in both these phosphors network [24].

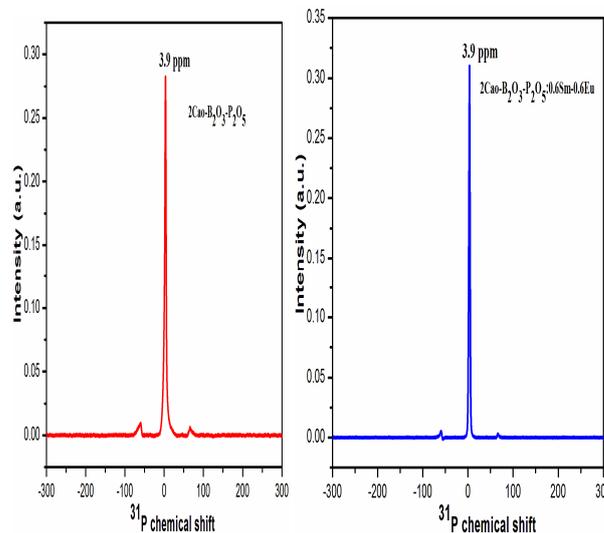


Fig 5  $^{31}\text{P}$  NMR spectra of  $2\text{CaO}\cdot\text{B}_2\text{O}_3\cdot\text{P}_2\text{O}_5$  and  $\text{Sm}^{3+}/\text{Eu}^{3+}$  co-doped  $2\text{CaO}\cdot\text{B}_2\text{O}_3\cdot\text{P}_2\text{O}_5$  phosphors.

### Photoluminescence spectra

Fig. 6 shows the comparison of excitation spectra of  $\text{Eu}^{3+}$  singly doped [17] and  $\text{Sm}^{3+}/\text{Eu}^{3+}$  co-doped phosphors monitoring the  $\text{Eu}^{3+}$  emission wavelength at  $613\text{ nm}$ .

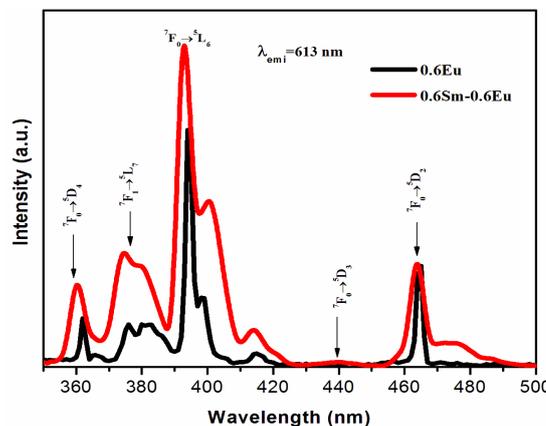


Fig 6 Excitation spectra of  $\text{Eu}^{3+}$  doped and  $\text{Sm}^{3+}/\text{Eu}^{3+}$  co-doped  $2\text{CaO}\cdot\text{B}_2\text{O}_3\cdot\text{P}_2\text{O}_5$  phosphors.

The excitation spectra of Eu<sup>3+</sup> doped phosphors display several excitation bands associated with transitions from the <sup>7</sup>F<sub>0</sub> and <sup>7</sup>F<sub>1</sub> states to <sup>5</sup>D<sub>4</sub>, <sup>5</sup>L<sub>7</sub>, <sup>5</sup>L<sub>6</sub>, <sup>5</sup>D<sub>3</sub> and <sup>5</sup>D<sub>2</sub> states as reported in previous paper [17]. It is observed that the spectrum of co-doped Sm<sup>3+</sup>/Eu<sup>3+</sup> phosphor also shows the same excitation bands which are observed for Eu<sup>3+</sup> doped phosphors.

The photoluminescence spectra of Sm<sup>3+</sup>/Eu<sup>3+</sup> co-doped CBP phosphors excited with 393 nm for different Sm<sup>3+</sup> concentrations are shown in Fig. 7.

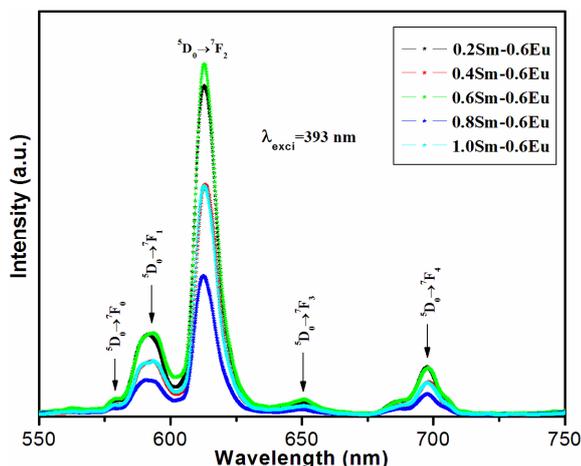


Fig 7 Emission spectra of Sm<sup>3+</sup>/Eu<sup>3+</sup> co-doped 2CaO-B<sub>2</sub>O<sub>3</sub>-P<sub>2</sub>O<sub>5</sub> phosphors for different concentrations.

This emission spectra consist five emission bands at 578, 592, 613, 650 and 698 nm, related to the <sup>5</sup>D<sub>0</sub>→<sup>7</sup>F<sub>J</sub> (J= 0, 1, 2, 3 and 4) transitions respectively. From the figure, it is observed that the intensity of emission peaks of Eu<sup>3+</sup> (613 nm) increased with Sm<sup>3+</sup> concentration upto 0.6 mol% and then decreased with increasing Sm<sup>3+</sup> concentration. The optimum concentration of Sm<sup>3+</sup> ion in Sm<sup>3+</sup>/Eu<sup>3+</sup> co-doped CBP phosphor was 0.6 mol% and it can be called concentration effect. In general, the sensitizer (donor) emission intensity decreases and activator emission intensity increases if energy transfer suited from sensitizer to activator (acceptor) in co-doped phosphors [25].

The energy transfer phenomenon from Sm<sup>3+</sup> to Eu<sup>3+</sup> can be explained using the energy level diagram as shown in Fig. 8.

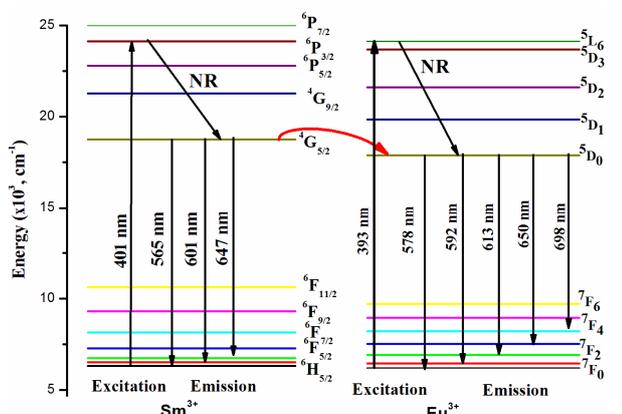


Fig 8 Partial energy level scheme of energy transfer from Sm<sup>3+</sup> to Eu<sup>3+</sup> in 2CaO-B<sub>2</sub>O<sub>3</sub>-P<sub>2</sub>O<sub>5</sub> phosphors.

From the figure, under the excitation of 401 nm, an electron in the ground state, <sup>6</sup>H<sub>5/2</sub> of Sm<sup>3+</sup> are stimulated to the excited

state <sup>6</sup>P<sub>3/2</sub> and then relaxes finally to the <sup>4</sup>G<sub>5/2</sub> level non-radiatively. The energy in the <sup>4</sup>G<sub>5/2</sub> level of Sm<sup>3+</sup> is transferred to the <sup>5</sup>D<sub>0</sub> level of Eu<sup>3+</sup> due to resonance (the <sup>4</sup>G<sub>5/2</sub> energy level of Sm<sup>3+</sup> is approximately 600 cm<sup>-1</sup> higher than the <sup>5</sup>D<sub>0</sub> level of Eu<sup>3+</sup>) between the two energy levels. The energy transfer from Sm<sup>3+</sup> to Eu<sup>3+</sup> is almost irreversible, because the <sup>4</sup>G<sub>5/2</sub> level in Sm<sup>3+</sup> is higher than the <sup>5</sup>D<sub>0</sub> level in Eu<sup>3+</sup>, and the probability of emitting phonons in Sm<sup>3+</sup>:<sup>4</sup>G<sub>5/2</sub>→Eu<sup>3+</sup>:<sup>5</sup>D<sub>0</sub> is higher than that of capturing phonons for Eu<sup>3+</sup>:<sup>5</sup>D<sub>0</sub>→Sm<sup>3+</sup>:<sup>4</sup>G<sub>5/2</sub> process. The resonance energy transfer increased the population of Eu<sup>3+</sup>: <sup>5</sup>D<sub>0</sub> level and it was due to the co-doping with Sm<sup>3+</sup> caused the sensitization of Eu<sup>3+</sup> emission under certain excitation conditions and lead to the expansion of the exciting range in Eu<sup>3+</sup> luminescence.

### Effect of thermal treatment on luminescence spectra

Sm<sup>3+</sup>/Eu<sup>3+</sup> co-doped present phosphor at optimum concentration are treated with different temperatures in the range 900 °C – 1100 °C with the step size of 50 °C to study the effect of temperature on Eu<sup>3+</sup> emission intensity. The measured emission spectra are shown in Fig. 9. From the figure it was observed that the Eu<sup>3+</sup> emission intensity increased from 900 °C to 950 °C then decreased upto 1050 °C and further increased at 1100 °C. The Eu<sup>3+</sup> emission intensity was maximum at 1100 °C and minimum at 900 °C. The splitting of magnetic dipole (<sup>5</sup>D<sub>0</sub>→<sup>7</sup>F<sub>1</sub>, 592 nm) and electric dipole (<sup>5</sup>D<sub>0</sub>→<sup>7</sup>F<sub>4</sub>, 698 nm) transitions is observed, for the 950 °C and 1100 °C temperatures. The splitting of these transitions might be due to change in the chemical environment surrounding and local environment of Eu<sup>3+</sup> ions [26].

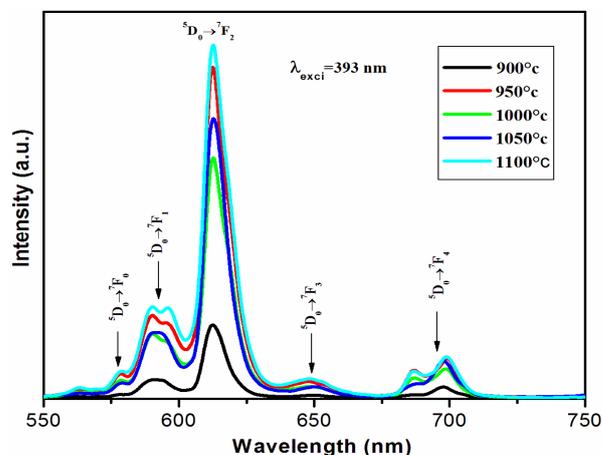


Fig 9 Emission spectra of 0.6Sm<sup>3+</sup>/0.6Eu<sup>3+</sup> co-doped 2CaO-B<sub>2</sub>O<sub>3</sub>-P<sub>2</sub>O<sub>5</sub> phosphors at different temperatures.

### Fluorescence decay

The fluorescence lifetime decay profiles of Sm<sup>3+</sup>/Eu<sup>3+</sup> co-doped CBP phosphor were measured with excitation wavelength 393 nm and emission wavelength 613 nm and are shown in Fig. 10. From the figure, it is noticed that the decay profiles exhibit non-exponential nature. The lifetimes (τ<sub>meas</sub>) of the excited state, <sup>5</sup>D<sub>0</sub> of Eu<sup>3+</sup> are obtained in this Sm<sup>3+</sup>/Eu<sup>3+</sup> co-doped CBP phosphors and are presented in Table 1. From the table, it is observed that the lifetime is higher (2.50 ms) for 0.6Sm<sup>3+</sup>/0.6Eu<sup>3+</sup> co-doped phosphor than the remaining phosphors and also higher than Eu<sup>3+</sup> singly doped CBP phosphor (2.30 ms) [17] indicating the energy transfer between the acceptor and donor ions. In the present work, the

concentration of  $\text{Sm}^{3+}$  (donor) ions per  $\text{Eu}^{3+}$  (acceptor) ion was found more, therefore the average distance between the Eu and Sm ions has decreased.

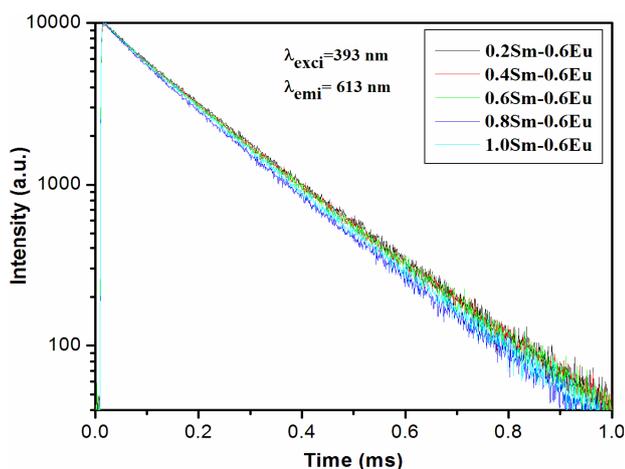


Fig 10 Decay curves of  $\text{Sm}^{3+}/\text{Eu}^{3+}$  co-doped  $2\text{CaO}\cdot\text{B}_2\text{O}_3\cdot\text{P}_2\text{O}_5$  phosphors.

Table 1 Measured lifetimes ( $\tau_{\text{cal}}$ , ms), absolute quantum efficiencies ( $Q_E$ , %) and color coordinates of  $\text{Sm}^{3+}/\text{Eu}^{3+}$  co-doped  $2\text{CaO}\cdot\text{B}_2\text{O}_3\cdot\text{P}_2\text{O}_5$  phosphor.

Formula	$\tau_{\text{meas}}$	$Q_E$	Color coordinates	
			x	y
$2\text{Ca}_{0.9}\text{O}\cdot\text{B}_2\text{O}_3\cdot\text{P}_2\text{O}_5:0.2\text{Sm}^{3+}/0.6\text{Eu}^{3+}$	2.21	97.22	0.59	0.30
$2\text{Ca}_{0.8}\text{O}\cdot\text{B}_2\text{O}_3\cdot\text{P}_2\text{O}_5:0.4\text{Sm}^{3+}/0.6\text{Eu}^{3+}$	2.25	75.18	0.62	0.33
$2\text{Ca}_{0.7}\text{O}\cdot\text{B}_2\text{O}_3\cdot\text{P}_2\text{O}_5:0.6\text{Sm}^{3+}/0.6\text{Eu}^{3+}$	2.50	59.38	0.65	0.32
$2\text{Ca}_{0.6}\text{O}\cdot\text{B}_2\text{O}_3\cdot\text{P}_2\text{O}_5:0.8\text{Sm}^{3+}/0.6\text{Eu}^{3+}$	2.32	42.50	0.63	0.31
$2\text{Ca}_{0.5}\text{O}\cdot\text{B}_2\text{O}_3\cdot\text{P}_2\text{O}_5:1.0\text{Sm}^{3+}/0.6\text{Eu}^{3+}$	2.29	28.02	0.60	0.32

Energy migration took place due to electronic multipole-multipole interactions and as a result, decay profiles exhibited non-exponential nature. The absolute quantum efficiencies (AQE) of  $\text{Sm}^{3+}/\text{Eu}^{3+}$  co-doped CBP phosphors were measured under excitation 393 nm with the fluorescence spectrometer using an integrating sphere and the AQE values are presented in Table 1. From the table, it is observed that AQE values have decreased with increasing  $\text{Sm}^{3+}$  concentration in  $\text{Sm}^{3+}/\text{Eu}^{3+}$  co-doped CBP phosphors.

#### Color chromaticity co-ordinates

The CIE chromaticity diagram of  $0.6\text{Sm}^{3+}/0.6\text{Eu}^{3+}$  co-doped CBP phosphor under the excitation of 393 nm was shown in Fig. 11.

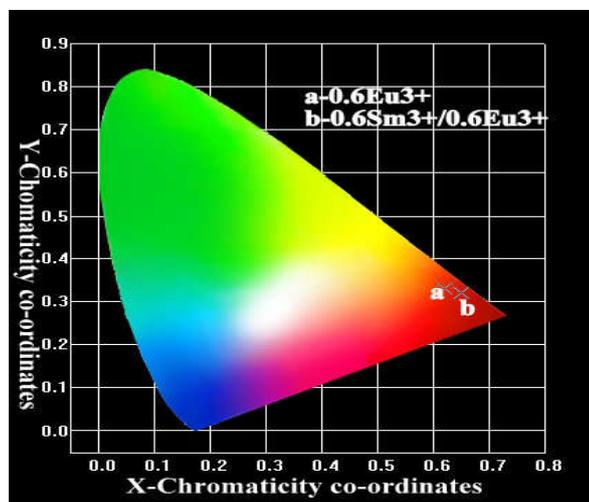


Fig 11 Color chromaticity diagram of  $\text{Eu}^{3+}$  doped and  $\text{Sm}^{3+}/\text{Eu}^{3+}$  co-doped  $2\text{CaO}\cdot\text{B}_2\text{O}_3\cdot\text{P}_2\text{O}_5$  phosphors.

The chromaticity coordinates of present phosphor with co-doped  $\text{Sm}^{3+}/\text{Eu}^{3+}$  ions for different concentrations were calculated and are presented in Table 1. The emitting color of  $\text{Eu}^{3+}$  (0.6 mol%) singly doped CBP phosphor [17] was in pale red region, and the corresponding color coordinates are 0.62 and 0.33. By doping  $0.6\text{Sm}^{3+}$  into the CBP phosphor, color coordinates shifted towards pure red region and the color coordinates was changed to 0.65 and 0.32. Hence,  $0.6\text{Sm}^{3+}/0.6\text{Eu}^{3+}$  co-doped CBP phosphor may be used as a potential red emitting material.

## CONCLUSIONS

$\text{Sm}^{3+}/\text{Eu}^{3+}$  co-doped calcium borophosphate phosphors were synthesized by solid state reaction method. XRD shows  $\text{Sm}^{3+}/\text{Eu}^{3+}$  ions occupy a site in nine coordinated large polyhedron occurring in tortuous vertical columns formed by  $\text{BO}_4$  and  $\text{PO}_4$  tetrahedra. The SEM images showed the particles were more irregular morphologies due to  $\text{Sm}^{3+}/\text{Eu}^{3+}$  incorporation. From the FT-IR spectrum, the prominent band at  $1029\text{ cm}^{-1}$  was due to the asymmetric stretching vibrations of  $[\text{PO}_4]^{3-}$  tetrahedrons. From  $^{31}\text{P}$  NMR spectra of  $\text{Sm}^{3+}/\text{Eu}^{3+}$  co-doped calcium borophosphate phosphors, the component lines corresponding to the chemical shifts located in the positive frequency region indicated the presence of mono-phosphate complexes  $\text{Q}^0\text{-(PO}_4^{3-})$ . From the photoluminescence spectra of  $\text{Sm}^{3+}/\text{Eu}^{3+}$  co-doped CBP phosphors, enhancement of emission intensity of  $\text{Eu}^{3+}$  was observed due to co-doping with  $\text{Sm}^{3+}$  ions and due to energy transfer process. The energy transfer mechanism, from  $\text{Sm}^{3+}$  to  $\text{Eu}^{3+}$  was clearly explained.  $\text{Eu}^{3+}$  ion emission intensities have significantly been enhanced due to sensitizer effect of  $\text{Sm}^{3+}$  ions in the  $\text{Sm}^{3+}/\text{Eu}^{3+}$  co-doped CBP phosphors. This phenomenon was clearly explained by partial energy level diagram. The energy transfer process was also evidenced by lifetime decay profiles. From CIE chromaticity diagram, pure red color emission was observed at  $0.6\text{Sm}^{3+}/0.6\text{Eu}^{3+}$  doped CBP phosphors. These results suggest that the prepared phosphors are the potential red luminescent optical materials.

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## References

1. Y. Shen, K. Qiu, W. Zhang, Y. Zeng, *Ceram. Int.*, 17 (2017) 30668-30675.
2. B. Bondzior, *J. Lumin.*, 173 (2016) 38-43.
3. J. Chen, Y. Zhao, Z. Mao, D. Wang, L. Bie, *Chem. Phys. Letters*, 669 (2017) 171-175.
4. K. Park, D. A. Hakeem, *Ceram. Int.*, 43 (2016) 4725-4729.
5. D. Pengpeng, *Ceram. Int.*, 43 (1) (2017) 1565-1570.
6. Z. Fu, L. Ma, S. Sahi, R. Hall, W. Chen, *J. Lumin.*, 143 (2013) 657-662.
7. L. Minhong, *J. Lumin.*, 2017, 184, 143-149.
8. A.N. Meza-Rocha, A. Speghini, M. Betteinelli, U. Caldino, *J. Lumin.*, 167 (2015) 305-310.
9. B.C. Joshi, *J. Non-Cryst. Solids*, 180 (1995) 217-220.

10. J. Qiu, M. Shojiya, Y. Kawamoto, K. Kadono, J. *Lumin*, 86 (2000) 23-31.
11. K.S. Lim, P. Babu, S.K. Lee, V.T. Pham, D.S. Hamilton, *J. Lumin*, 737 (2003) 102–103.
12. X. Min, Z. Huang, M. Fang, Y.-G. Liu, C. Tang, X. Wu, *Inorg. Chem*, 2014, 53, 6060-6065.
13. A. Mantwa Lephoto, G. Kamohelo, Tshabalala, J. Selepe, Motlounq, Iorkyaa Ahemen, M. Odireleng, Ntwaeaborw, *Physica B*, 2017, <https://doi.org/10.1016/j.physb.2017.06.063>.
14. S. Hachani, B.Moine, A.El-akrmi, M.Ferid, *J. Lumin*, 130 (2010) 1774-1783.
15. Bi. Wenbo, Q. Meng, W. Sun, *Ceram. Int*, 12 (2016) 14086-14093.
16. F. Kang, Y. Hu, H. Wu, Z. Mu, G. Ju, C. Fu, N. Li, *J. Lumin*, 132 (2012) 887-894.
17. V. Reddy Prasad, S. Damodaraiah, S. Babu, Y.C. Ratnakaram, *J. Lumin*, 187 (2017) 360-367.
18. L. Pierron, A. Kahn-Harari, B. Viana, P. Dorenbos, C.W.E. Van Eijk, *J. Phys. Chem. Solids*, 64 (2013) 1743-1748.
19. A.M. Srivastava, *J. Lumin*, 1998, 78, 239-243.
20. Chapter 4.1 of B.Streetman, *Solid-State Electronic Devices*, 4th Edition, Prentice-Hall, 1995.
21. V.N. Rai, B.N. Rajshekhar, S. Kher, S.K. Deb, *J. Lumin*. 130 (2010) 582-586.
22. V.B. Taxak, S. Dayawati, S.P. Khatkar, *Curr. Appl. Phys*, 13 (2013) 594-598.
23. R.K. Brow, D.R. Tallant, S.T. Meyers, and C.C. Phifer, *J. Non-Cryst. Solids*, 191 (1995) 45-55.
24. M. Szumera, *Spectro. Chim. Acta A*, 137 (2015) 111-115.
25. S. Damodaraiah, V. Reddy Prasad, S. Babu, Y.C. Ratnakaram, *Opt. Mater*, 67 (2017) 14-24.
26. K. Binnemans, C. Gorller-Walrand, *J. Rare. Earths*, 14 (1996) 173-177.

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