

## Photoluminescence of – $\text{Ca}_9\text{Al}(\text{PO}_4)_7 : \text{Eu}^{3+}$ phosphor

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### ABSTRACT

$\text{Eu}^{3+}$  activated  $\text{Ca}_9\text{Al}(\text{PO}_4)_7 : x\text{Eu}^{3+}$  (CALP: $x\text{Eu}^{3+}$ ) samples were prepared in the present work. These compounds were prepared in different concentrations of  $\text{Eu}^{3+}$  by combustion synthesis. Photoluminescence and CIE Colour co-ordinates characterization were studied. Data of excitation spectra reveal that the energy band from 380 nm to 410 nm appears at high intensity. The highest luminescence emission intensity was found at 1 mole% of  $\text{Eu}^{3+}$ . A concentration of one mole percent  $\text{Eu}^{3+}$  ions was found to be optimal, and red light is emitted from the phosphor which is located at (0.677,0.322) in CIE coordinates. As CALP: $x\text{Eu}^{3+}$  provides red emission which helps in solving colour rendering index.

Keywords : Red Phosphor, Rare doped, CIE coordinates, Combustion synthesis

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## I. INTRODUCTION

Nowadays, researchers are showing more interest in the development of ecofriendly and energy efficient light sources. For this new phosphor materials are in growing demand. This leads to a closer and detailed look at luminescence properties with more optical applications. Functional materials of rare-earth(RE) co-doped or doped ions, with excellent luminescent results, are being studied widely for the potential applications [i] [ii] [iii]. Among these elements, europium is the most commonly used activator for phosphor materials as well as a red emitter.  $\text{Eu}^{3+}$  activated phosphors like, phosphates, aluminates, silicates and derivatives, for luminescent properties are being studied intensively and used for optical display field [iv]. Because of characteristic optical

properties of the synthesized  $\text{Eu}^{3+}$  doped phosphors they are widely applicable in Plant growth LEDs [v]. Optical thermometer applications [vi] [vii], photocatalysis [viii], fingerprint detection and anti-counterfeiting[ix], Biological Probes [x] [xi]. The decay time of  $\text{Eu}^{3+}$  containing  $\text{Ca}_9\text{Al}(\text{PO}_4)_7$  phosphor shows long decay time approximately 150 times to that of  $\text{Eu}^{3+}$  [xii]. The present study emphasized on mainly the synthesis of  $\text{Eu}^{3+}$  containing  $\text{Ca}_9\text{Al}(\text{PO}_4)_7$ . PL characterization consist of excitation and emission.

## II. Experimental

$\text{Eu}^{3+}$  activated  $\text{Ca}_9\text{Al}(\text{PO}_4)_7 : x\text{Eu}^{3+}$  (CALP: $x\text{Eu}^{3+}$ ) samples were prepared as follows: Firstly, stoichiometric quantity of source materials  $\text{NH}_4\text{H}_2\text{PO}_4$  (A.R.),  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  (A.R.) and  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  (A.R.),

were mixed thoroughly and required amount of  $\text{CO}(\text{NH}_2)_2$  (A.R.) was added as fuel and this is treated as mixture 1. Then  $\text{Eu}_2\text{O}_3$  (A.R.) was dissolved in dilute  $\text{HNO}_3$  to convert into  $\text{Eu}(\text{NO}_3)_3$  completely and this is added in mixture 1. The whole mixture was introduced into muffle furnace which was maintained at  $520^\circ\text{C}$  for 10 min. Then these samples were reheated at  $650^\circ\text{C}$  for 3 hours and were allowed to cool to reach room temperature. Finalize the preparation of the sample by crushing it into a fine powder to characterize the photoluminescence properties. The measurements of excitation (PLE) and Spectrums of emission (PL) were performed by using a Shimadzu RF 5301 PC (Japan) Spectrofluorophotometer and for excitation, source was used as xenon lamp. For Analysis, all characterizations were made at room temperature by keeping identical instrumental parameters.

### III. Results and discussion

#### Photoluminescence properties

Emission spectra at the room temperature of the crystal  $\text{Ca}_9\text{Al}(\text{PO}_4)_7$  doped with different concentrations of  $\text{Eu}^{3+}$  is shown in figure 1. For the PL excitation, light of 395 nm is used. The prepared crystal emitted the red wavelength of varying intensities, which confirmed the  $\text{Eu}^{3+}$  as activator had successfully settled into the host lattice of  $\text{Ca}_9\text{Al}(\text{PO}_4)_7$ . The strong and sharp peaks at 593 and 614 nm were observed related to transitions  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$  and  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$  respectively. These transitions are the specific characteristic emissions of  $\text{Eu}^{3+}$ . While the  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$  transition is well known to be primarily a magnetic dipole transition when the  $\text{Eu}^{3+}$  ions are in high symmetry positions, the  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$  transitions are essentially electric dipole transitions that occur only when the  $\text{Eu}^{3+}$  ions are in locations without inversion symmetry<sup>[xiii]</sup>. As the doping concentration increases from 0.1mol% to 1mol%, the emission intensities of the peaks also rise and after that decreases. General expectation is that photoluminescence (PL) increases

with the increase in the concentration of  $\text{Eu}^{3+}$  ions. Concentration quenching occurs above 1mol% of  $\text{Eu}^{3+}$  ions. Due to this decrease in emission intensity is observed. Higher concentration of  $\text{Eu}^{3+}$  ions results in non-radiative interaction among ions, this results in the more resonant energy transfer. The higher concentration leads to decrease in the distance between  $\text{Eu}^{3+}$  ions, which makes transfer of energy by resonance process from one ion to other ion more easily, the energy eventually reaches a trap from which it is dissipated by non-radiative processes rather than by the emission of visible light<sup>[xiv]</sup> <sup>[xv]</sup>. In the  $\text{Ca}_9\text{Al}(\text{PO}_4)_7:1\text{mol}\% \text{Eu}^{3+}$ , the intensity of  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$  transition intensity is at 614 nm which is dominant to  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$  transition intensity at 593 nm. The transition  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_2$  is dominant over the transition  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$ , which indicates that  $\text{Eu}^{3+}$  ions are present in an asymmetric local environment<sup>[xvi]</sup>. It is observed that magnetic dipole transition of the same kind i.e.  ${}^5\text{D}_0 \rightarrow {}^7\text{F}_1$  was obtained for  $\text{Eu}^{3+}$  ions doped  $\text{Sr}_2\text{LiScB}_4\text{O}_{10}$ ,  $\text{LiYGeO}_4$ , and  $\text{CaMoO}_4$  phosphors<sup>[xvii]</sup> <sup>[xviii]</sup> <sup>[xix]</sup>. The photoluminescence excitation behavior of the prepared  $\text{Eu}^{3+}$  ions doped CALP phosphors had been studied by recording characterization spectra. CALP phosphor excitation spectrum is recorded for  $\text{Eu}^{3+}$  ions. A high intense excitation band of  ${}^7\text{F}_0 \rightarrow {}^5\text{L}_6$  transition was observed at 395 nm. From the data of excitation spectra, it was noted that excitation band from 380 nm to 410 nm is appeared at high intensity. The diagram showing various transition in energy level.

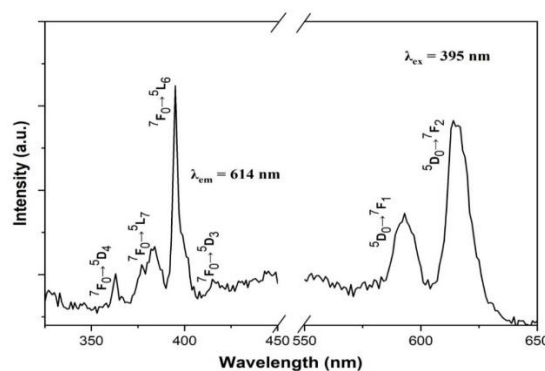


Fig. 1 : The Photoluminescence excitation and emission spectra of the red-emitting phosphors

Ca<sub>9</sub>Al(PO<sub>4</sub>)<sub>7</sub>:Eu<sup>3+</sup> ( $\lambda_{ex}$ = 395nm,  $\lambda_{em}$  =613 nm) at 650°K

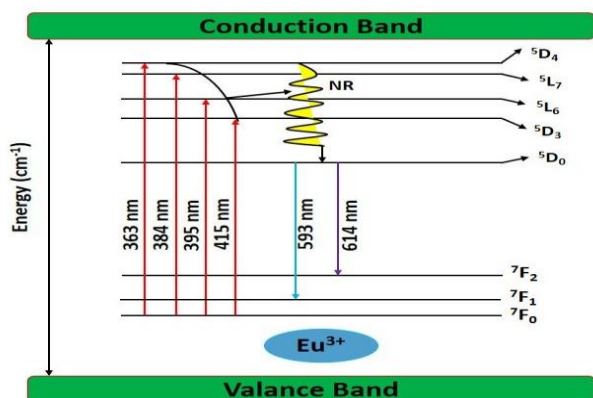


Fig.2 : Energy level diagram showing emission and excitation transitions for Eu<sup>3+</sup> doped Ca<sub>9</sub>Al(PO<sub>4</sub>)<sub>7</sub>

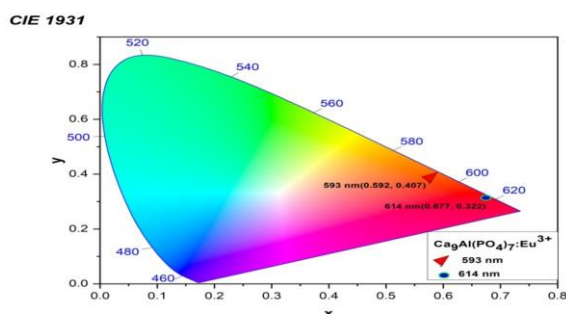


Fig.3 : CIE colour chromaticity coordinate diagram for Eu<sup>3+</sup> CaAlP

Materials performance: Colour coordinates (CIE)

Using standard procedures, the chromaticity coordinates of 1.0 mol% doped sample annealed at 650°C at CIE standard temperature were determined. The values of x and y coordinates of the system were calculated to be (0.592, 0.407), (0.677,0.322) corresponds to 593 nm and 613 nm respectively. The CIE diagram shown in Figure shows ● , point for the 'red emission' given by Ca<sub>9</sub>Al(PO<sub>4</sub>)<sub>7</sub> doped with Eu<sup>3+</sup>[xx].

#### IV. Conclusion

The emission spectra at 614 nm for transition <sup>5</sup>D<sub>0</sub> → <sup>7</sup>F<sub>2</sub> was highly intensified for CAIP:Eu<sup>3+</sup> material. It was also noted that, the emission intensity for transition <sup>5</sup>D<sub>0</sub> → <sup>7</sup>F<sub>2</sub> at 614nm dominant over transition <sup>5</sup>D<sub>0</sub> →

<sup>7</sup>F<sub>1</sub> at 593 nm. At excitation transition was noted at 395 nm The CAIP:Eu<sup>3+</sup> material of very high luminescence red emission of nearly 614 nm is definitely a display applications material for investigation further use.

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