Eu and Dy activated (Sr_{0.90} Ca_{0.10})_3(PO_4)_2 phosphors for near-UV LED

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Abstract. The new efficient trivalent Eu and Dy activated (Sr_{0.90} Ca_{0.10})_3(PO_4)_2 phosphors were prepared by the conventional solid state method. X-ray powder diffraction analysis confirmed the formation of (Sr_{0.90} Ca_{0.10})_3(PO_4)_2 host lattice. The Eu³⁺ PL emission spectrum was observed in (Sr_{0.90} Ca_{0.10})_3(PO_4)_2 phosphors at 590 (orange) and 614 nm (red) region, the spectrum due to ⁵D₀→⁷F₁ and ⁵D₀→⁷F₂ transitions at near UV excitation, respectively. (Sr_{0.90} Ca_{0.10})_3(PO_4)_2: Dy³⁺ excited by 350 nm near-ultraviolet (NUV) light, the phosphors show an efficient blue and yellow band emissions, which originates from the ⁵F_{9/2}→⁷H_{15/2} and ⁵F_{9/2}→⁷H_{13/2} transitions of Dy³⁺ ion, respectively. The excitation spectra of the phosphors are broadband extending from 340 to 400 nm, which are characteristics of NUV excited LED. The investigated prepared phosphors are suitable for a NUV excited LED.

1. Introduction:
White-light emitting diodes are one of the most promising eco-friendly light sources, with low energy consumption [1]. As environmental subject has become serious, the need for mercury-free fluorescent lamps for general lighting has become an important subject for light source manufacturers. As it is possible to improve the luminous efficiency of white light LEDs excited by near-UV LEDs in the near-UV to blue part of the spectrum [2] around 380–420 nm, researchers worldwide have been investigating other suitable chemical compounds for solid-state lighting. Recently, Dhoble and co-workers reported some phosphate based Eu³⁺ and Dy³⁺ activated M₂(PO₄)₃F (M= Ba, Sr, Ca) [3], K₃Al₂(PO₄)₃ [4], NaₓX(PO₄)F (X = Mg, Ca, Sr) [5] and NaCaPO₄ [6] phosphors for lamp industry.

With respect to the phosphors presently used in white LED systems, most do not meet the optimum requirements. Accordingly, novel luminescent materials with improved properties are greatly in demand. In this article we report on the synthesis and characterization of Eu and Dy activated (Sr_{0.90} Ca_{0.10})_3(PO_4)_2 phosphors were prepared by the conventional solid state method. The X-ray diffraction (XRD) and photo luminescent (PL) properties of these phosphors were investigated at room temperature.

2. Experimental:
Trivalent Eu and Dy activated (Sr_{0.90} Ca_{0.10})_3(PO_4)_2 phosphate based phosphors were synthesized by the solid state method. The starting materials SrCO₃, CaCO₃ and NH₄H₂PO₄ of analytical grade (pure) were used. These materials were weighed in the proper molar ratio and then Dy₂O₃ was introduced as a dopant followed by mixing and grinding homogeneously in an agate mortar. The mixture was heated at 500°C in a silica crucible for 2 h. The vapors extraneous to the desired product that was evolved during the process were allowed to be released. After grinding, the mixture was heated at 800 °C for 24 h, thereby obtaining the white phosphor powder. Similar procedure was followed for Eu activated (Sr_{0.90} Ca_{0.10})_3(PO_4)_2.
The prepared host lattice was characterized for their phase purity and crystallinity by X-ray powder diffraction (XRD) using PAN-analytical diffractometer (Cu-Kα radiation) at a scanning step of 0.01°, continue time 20s, in the 2θ range from 10° to 80°; the average crystallite size was calculated from the broadening of the X-ray line (311) using Scherer’s equation. The photoluminescence measurement of excitation and emission were recorded on the Shimadzu RF5301PC spectrofluorophotometer. The same amount of sample (2g) was used for each measurement. Emission and excitation spectra were recorded using a spectral slit width of 1.5 nm.

3. Results and discussion:

3.1 XRD

Figure 1 shows the XRD pattern and XRD did not show the presence of the starting constituents and other likely phases which is an indirect evidence for the formation of the desired compound. The XRD pattern of \(\text{Sr}_{0.90}\text{Ca}_{0.10}\text{PO}_4\text{)}_2\) and it agrees well with JCPDS no. 00-14-0205. This shows final product was formed in crystalline, homogeneous form and solid state reaction of the mixtures took place well.

![Figure 1: XRD pattern of \(\text{Sr}_{0.90}\text{Ca}_{0.10}\text{PO}_4\text{)}_2\)](image)

3.2 The excitation and emission spectra of \(\text{Sr}_{0.90}\text{Ca}_{0.10}\text{PO}_4\text{)}_2\):\(\text{Eu}^{3+}\)

Figure 2(a) shows the PL excitation spectrum of the \(\text{Sr}_{0.90}\text{Ca}_{0.10}\text{PO}_4\text{)}_2\):\(\text{Eu}^{3+}\) phosphor. There are two excitation bands are observed at 342 and 394 nm, which are all caused by the f–f transitions. Both are observed with a maximum intensity at 394 nm (stronger excitation band). Under the excitation of 394 nm, the phosphor of \(\text{Sr}_{0.90}\text{Ca}_{0.10}\text{PO}_4\text{)}_2\):\(\text{Eu}^{3+}\) has two sharp orange/red-emission bands at 590 and 614 nm shown in figure 2(b).

![Figure 2(a): Excitation spectrum \(\text{Sr}_{0.90}\text{Ca}_{0.10}\text{PO}_4\text{)}_2\):\(\text{Eu}^{3+}\)](image)

![Figure 2(b): Emission spectra of \(\text{Sr}_{0.90}\text{Ca}_{0.10}\text{PO}_4\text{)}_2\):\(\text{Eu}^{3+}\)](image)
Among these two emission bands the 614 nm is corresponding to the electric-dipole transition $^5D_0 \rightarrow ^7F_2$ of Eu$^{3+}$ whereas other is corresponding to the magnetic dipole transition $^5D_0 \rightarrow ^7F_1$ of Eu$^{3+}$ ion which is the less prominent, these two peaks are obtained due to the splitting of Eu$^{3+}$ ion emission. The luminescent properties of Eu$^{3+}$ ion in the crystalline $(Sr_{0.90}Ca_{0.10})_3(PO_4)_2$ phosphor are in good agreement with those obtained through other processes indicating that Eu$^{3+}$ ions have been effectively doped into the host lattice of $(Sr_{0.90}Ca_{0.10})_3(PO_4)_2$. The PL intensity increased with concentration from 0.1–1 mol% and it decreased at more than 1 mol% probably due to concentration quenching effect. In present case, the low contributions of the orange $^5D_0 \rightarrow ^7F_1$ emissions and the high intensity of the red $^5D_0 \rightarrow ^7F_2$ emission results in high colour purities that is adequate for near UVLED applications.

3.3 The excitation and emission spectra of $(Sr_{0.90}Ca_{0.10})_3(PO_4)_2$:Dy$^{3+}$

The intense excitation peak is observed at 349 nm and other weak peaks are also observed at 325 nm to 387 nm shown in figure 3(a) and only emission intensity vary with respect to all three excitation wavelengths. In this context, excitation curve 350 nm peak is near UV excitation which is more applicable (i.e. 385 to 395 nm) for UVLED phosphor. Accordingly, out of all three peaks we select the 350 nm peak for excitation in the experimental work. The emission spectrum shown in figure 3(b) and all the samples have the two emission bands: one is centered at 485 nm (blue) and another is at 575 nm (yellow). They are assigned to the Dy$^{3+}$ electronic transitions of $^{4}F_{9/2} \rightarrow ^{6}H_{15/2}$ and $^{4}H_{13/2}$ energy levels, respectively. A series of $(Sr_{0.90}Ca_{0.10})_3(PO_4)_2$:Dy$^{3+}$ phosphor with various Dy$^{3+}$ concentrations ($x=0.1$ mol % − 1 mol %) were prepared and the effect of doped Dy$^{3+}$ concentration on the emission intensity of was investigated.

![Figure 3(a): Excitation spectrum of $(Sr_{0.90}Ca_{0.10})_3(PO_4)_2$:Dy$^{3+}$](image_url)

![Figure 3(b): Emission spectra of $(Sr_{0.90}Ca_{0.10})_3(PO_4)_2$:Dy$^{3+}$](image_url)

Thus the combination of colors gives BYR (blue–yellow–red) emissions which can produce white light, by near UV excitation. $(Sr_{0.90}Ca_{0.10})_3(PO_4)_2$: activated with Dy$^{3+}$ and Eu$^{3+}$ ions phosphors exhibit a strong absorption in the range of 340–400 nm and chromatic properties indicated that present phosphor is a promising candidate for producing near ultraviolet white light-emitting diodes (near-UV LED).

4. Conclusions:
In summary, the Eu$^{3+}$ and Dy$^{3+}$ ions activated $(Sr_{0.90}Ca_{0.10})_3(PO_4)_2$ phosphors have been synthesized by the solid state method. The formation of these compounds was confirmed by the XRD technique. The photoluminescence characterization of prepared phosphors show role of rare ions in the host lattice. The PL spectroscopic characterizations of the prepared phosphors are done using excitation and emission spectra. Under near UV excitation (350 nm) $(Sr_{0.90}Ca_{0.10})_3(PO_4)_2$:Eu$^{3+}$ the emission...
spectrum shows peaks at 590 nm (orange) while other are at 614 nm (red). When \((\text{Sr}_{0.90}\text{Ca}_{0.10})_3(\text{PO}_4)_2 :\text{Dy}^{3+}\) phosphor excited at 350 nm the emission spectrum shows intense bands at 485 nm (blue), and 575 nm (yellow). Both \(\text{Eu}^{3+}\) and \(\text{Dy}^{3+}\) activated \((\text{Sr}_{0.90}\text{Ca}_{0.10})_3(\text{PO}_4)_2\) phosphors show the excitation in the range of 340-390 nm of near UVLED excitation and emission observed in the red and blue/yellow region of the spectrum. This results show the \((\text{Sr}_{0.90}\text{Ca}_{0.10})_3(\text{PO}_4)_2 :\text{Eu}^{3+}\) and \((\text{Sr}_{0.90}\text{Ca}_{0.10})_3(\text{PO}_4)_2 :\text{Dy}^{3+}\) phosphors could be applicable for near UVLED phosphors.

References:
[1] Mikami M, Watanabe H, Uhedra K, Shimooka S, Shimomura Y, Kurushima T, 2009 *IOP Conf Ser: Mater Sci Eng* **1** 012002.
[2] Yamada M, Narukawa Y, Mukai T, 2002 *Jpn. J. Appl. Phys.*, **41** L246.
[3] Nagpure I M, Shinde K N, Dhoble S J, Kumar Animesh, 2009 *J Alloys Compd.*, **481** 632.
[4] Shinde K N, Dhoble S J, 2011 *J. Fluoresc* **21** 2053.
[5] Dhoble S J, Pawade V B, Shinde K N, 2010 *Eur. Phys. J. Appl. Phys.* **52** 11104.
[6] Shinde K N, Dhoble S J, Kumar Animesh, 2011 *J. Rare Earths*, **29(6)** 527.