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Red Emitting Caal$_3$(PO$_4$)$_3$F$_2$:Eu^{3+} Phosphor for White Light Emitting Diodes

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ABSTRACT

The Red-emitting phosphors of Eu^{3+} activated phosphate based phosphors prepared by combustion synthesis, characterized by XRD (X-ray diffraction), SEM (Scanning electron microscopy) and Photoluminescence (PL) techniques, has been reported. The luminescence properties were investigated by photoluminescence excitation and emission spectra. PL excitation spectrum of CaAl$_3$(PO$_4$)$_3$F$_2$:Eu^{3+} phosphors shows the excitation peaks ranging from 370 to 400 nm due to 4f→4f transitions of Eu^{3+} ions. PL emission spectrum of Eu^{3+} ion under 394 nm excitation gives PL emission at 615 nm (red) due to $^5D_0 \rightarrow {}^7F_2$ transitions, 593 nm (orange) emission due to $^5D_0 \rightarrow {}^7F_1$transitions. Hence PL emission in trivalent europium may be efficient photoluminescent materials for solid-state lighting phosphors.

Keywords: Luminescence, X-ray diffraction, LED & HaloPhosphate.

I. INTRODUCTION

Over the past two decades, there has been considerable research in the lighting community in an effort to fabricate white light sources using InGaN based LEDs.

It is expected that these solid state light sources will eventually replace existing lighting technologies [1, 2]. White Lighting emitting diodes (WLEDs) have attracted great interests for general illumination because LEDs have advantages over the existing incandescent and halogen lamps in terms of power efficiency, reliability and long lifetime etc [3]. Halophosphate As an important family of luminescent materials, halophosphate have been paid intense attention because of their excellent properties. Among halo based phosphors, halophosphate phosphors have attracted tremendous attention due to their intense luminescence intensities, high emission efficiencies and wide application fields in displays and UV devices [4-9].

White LEDs in which a near UV-LED is combined with blue, green, and red phosphors have been investigated due to less current droop and improved binning of the UV-LEDs, and a better control over color rendering index and color temperature through manipulation of phosphor blends. [10-12] .

In this article for red-emitting phosphors with high efficiency and proper CIE chromaticity coordinates, the Eu^{3+} activated phosphors are primarily considered. The major emission of Eu^{3+} usually shows an intense orange light or red due to the transition of $^5D_0 \rightarrow {}^7F_1$ or $^5D_0 \rightarrow {}^7F_2$, which depends on the structure of the phosphor host, and it mainly shows sharp $^5D_0 \rightarrow {}^7F_2$ red-emission lines around 610–625 nm when Eu^{3+} ions occupy the lattice sites without centro-symmetry. To find novel efficient red emitting LED phosphors, the choice of the host is another key factor. Phosphate compounds have been widely studied due to their stability, various crystal structures, and relatively easy preparation [13].White light LED is in high demand for the solid-state lighting technology because the most challenging application for white light LED is the replacement of conventional incandescent and fluorescent lamps [14].
Accordingly, novel luminescent materials with improved properties are greatly in demand. In this paper, the phosphate CaAl$_3$(PO$_4$)$_3$F$_2$:Eu^{3+} and Eu^{3+} phosphors were

synthesized by the combustion method and its luminescent properties were also investigated.

II. METHODS AND MATERIAL

Eu^{3+} activated $CaAl_3(PO_4)_3F_2$ phosphors were prepared via combustion synthesis. The starting AR grade materials (99.99% purity) were taken where Calcium nitrate $(CaNO_3)_2$, Aluminum nitrate $[Al(NO_3)_3.9H_2O]$, Ammonium di-hydrogen phosphate $NH_4H_2(PO_4)$, Europium oxide (Eu_2O_3), Ammonium fluoride (NH_4F) and urea used as fuel. In the present investigation, materials were prepared according to the chemical formula $CaAl_{3-x}(PO_4)_3F_2{:}Eu_x$ ($0.1 \le x \le 1.0$). Eu^{3+} ions were introduced as $Eu(NO_3)_3$ solutions by dissolving Eu_2O_3 into dil. HNO_3 solution for the preparation of $CaAl_{3-x}(PO_4)_3F_2{:}Eu_x$ ($0.1 \le x \le 1.0$) phosphor. After mixing all reagents for about 15 min, mixture was transferred to a furnace preheated at 650^0C and the porous products were obtained. The photoluminescence measurement of excitation and emission were recorded on the Shimadzu RF5301PC spectrofluorophotometer. Emission and excitation spectra were recorded using a spectral slit width of 1.5 nm. The prepared host lattice was characterized for its phase purity and crystallinity by X-ray powder diffraction (XRD), using a PAN-analytical diffractometer (Cu–Kα radiation) .

III. RESULTS AND DISCUSSION

XRD analysis of $CaAl_3(PO_4)_3F_2{:}Eu^{3+}$ phosphor

X-ray diffraction (XRD)

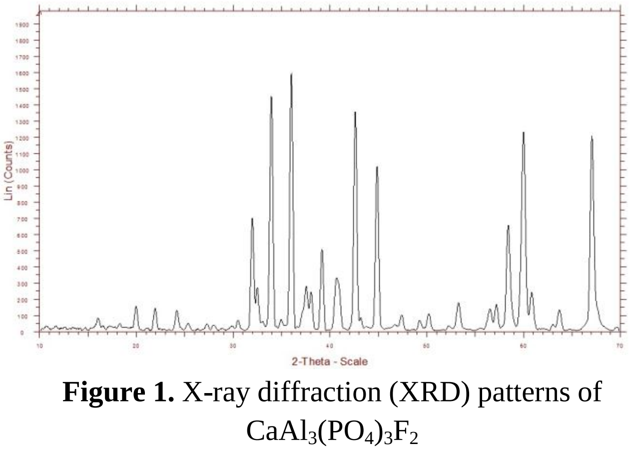

Figure 1. X-ray diffraction (XRD) patterns of $CaAl_3(PO_4)_3F_2$
phosphor powder.

The XRD pattern of the powder was recorded on an X-ray diffractometer using Cu-Kα radiation (1.54060 nm) and at a scanning scan step time of 10.3377 s. Figure 1. show the XRD pattern of $CaAl_3(PO_4)_3F_2$ prepared at 650 °C combustion synthesis. However, the obtained diffraction peaks of compound does not match any data in the JCPDS base after careful comparison with the reported compounds, considering that the starting materials are weight according to the given chemical composition of $CaAl_3(PO_4)_3F_2$ matrix, they are thereby named as $CaAl_{3-x}(PO_4)_3F_2{:}Eu_x$ ($0.1 \le x \le 1.0$) phosphor in this paper. The XRD pattern did not indicate presence of the constituents like, $(CaNO_3)_2$, $Al(NO_3)_3.9H_2O$, NH_4H_2 (PO_4), (NH_4F), Eu_2O_3 and other likely phases, which are an indirect evidence for the formation of the desired compound. These results indicate that the final product was formed in crystalline and homogeneous form. Prepared compounds XRDs data not available in standards JCPDs file. However, some new diffraction peaks also emerge, which are characteristic diffraction peaks for the prepared samples, but cannot be attributed to any known compounds.

Scanning electron microscopy (SEM):

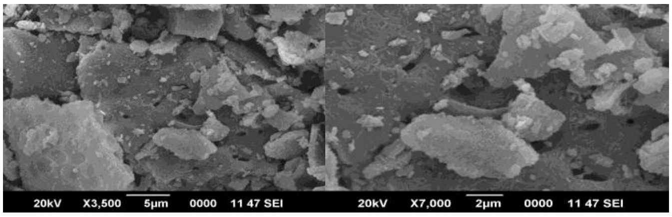

Figure 2. SEM patterns of $CaAl_3(PO_4)_3F_2{:}Eu^{3+}$ phosphor powder.

The particle size distribution of the phosphor is an important factor for its application in WLEDs. Figure 2. Show the SEM images of $CaAl_{3-x}(PO_4)_3F_2{:}Eu_x$ ($0.1 \le x \le 1.0$) phosphors with various concentrations of Eu^{3+} ions prepared by combustion synthesis at 650 ^{0}C. A SEM study was carried out to investigate the surface morphology and crystallite sizes of the $CaAl_{3-x}(PO_4)_3F_2{:}Eu_x$ ($0.1 \le x \le 1.0$) phosphor powders. An average crystallite size is in the sub-micrometer range (2-5µm). These sub-micrometers $CaAl_3(PO_4)_3F_2{:}Eu^{3+}$ phosphor plausibly suitable for coating purpose in lighting industry particularly, in solid state lighting [15]. In the combustion synthetic process, we found the optimal shape and size of the phosphor using only the synthetic temperature. The surfaces of the foam showed many cracks and pores formed by the escaping gases during the combustion reaction. Most particles showed sizes of a few micrometers. These results indicate that the final product is in crystalline forms. Typical morphological images are represented in Figure 2. The particles possess foam-like morphology. Combustion synthesis is a method based on the principle that once a reaction is initiated under heating, an exothermic reaction occurs that becomes self-sustaining within a certain time interval, resulting in a powder as final product, so solution combustion synthesis has the advantage of rapidly producing fine and homogeneous powders.

Photo luminescent properties of $CaAl_{3-x}(PO_4)_3F_2$: Eu_x^{3+} (0.1 ≤ x ≤ 1.0)

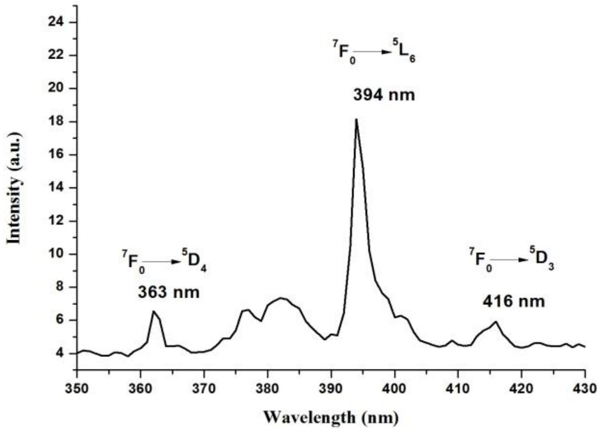

Figure 3. Excitation spectrum $CaAl_3(PO_4)_3F_2$: Eu^{3+} phosphor monitored at 617 nm

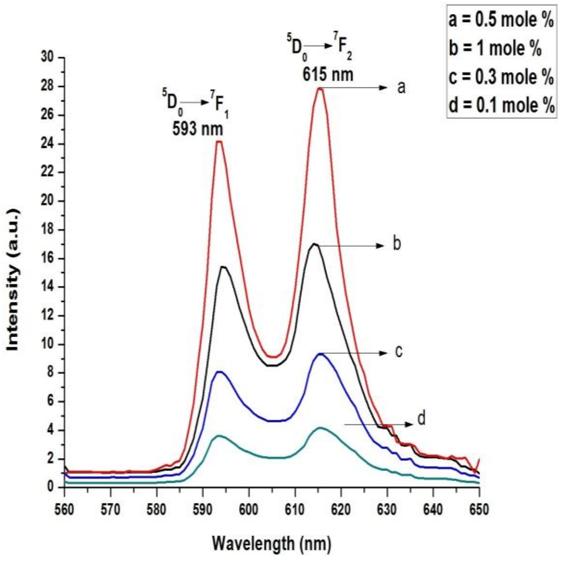

Figure 4. Emission spectra of $CaAl_{3-x}(PO_4)_3F_2$: Eu_x^{3+} phosphor (0.1 ≤ x ≤ 1.0) (excited at 394 nm).

The excitation spectrum by monitoring $^5D_0 \rightarrow ^7F_2$ emission of Eu^{3+} in $CaAl_3(PO_4)_3F_2$: Eu^{3+} phosphor is given in Figure 3. The narrow peaks located at wavelengths longer than 394nm, which is caused by the characteristic $^7F_0 \rightarrow ^5L_6$ transition of Eu^{3+} [16]. From the spectrum, it was found that the intensity of f–f transition at 394 nm is high compared with the other transitions and has been chosen for the measurement of emission spectra of $CaAl_3(PO_4)_3F_2$:Eu^{3+}phosphors. The most intense peak obtained at 394 nm clearly suggests that these phosphors are effectively excited by near ultra violet light emitting diodes (NUV-LEDs) [17]. Figure 3.

In the wavelength region 350–430 nm, several excitation peaks are observed and located at 363 nm ($^7F_0 \rightarrow ^5D_4$), 394 nm ($^7F_0 \rightarrow ^5L_6$), and 416 nm ($^7F_0 \rightarrow ^5D_3$) which are assigned to 4f–4f transitions within the Eu^{3+} in the host lattice [18]. Figure 4. shows the emission spectra of $CaAl_{3-x}(PO_4)_3F_2$:Eu_x^{3+} (0.1 ≤ x ≤ 1.0) under direct excitation the $^7F_0$–$^5L_6$ transition of Eu^{3+} at 394 nm. The $CaAl_{3-x}(PO_4)_3F_2$:Eu_x^{3+} (0.1 ≤ x ≤ 1.0) is composed of a series of linear spectra. Typical linear emission peaks of Eu^{3+} can be observed in the range of 575–650 nm and ascribed to the transition $^5D_0$ level to $^7F_1$, $^7F_2$ levels of Eu^{3+}, respectively [19]. The emission spectra of $CaAl_{3-x}(PO_4)_3F_2$:Eu_x^{3+} (0.1 ≤ x ≤ 1.0) phosphor in general, Eu^{3+} has dominant peaks in the emission spectra in many host matrices. The peaks located at 615 (red) corresponds to the hypersensitive transition $^5D_0 \rightarrow ^7F_2$ (615 nm) and another peaks located at 593 nm (red-orange) is due to the transition $^5D_0 \rightarrow ^7F_1$ (593 nm). It is well-known that the $^5D_0 \rightarrow ^7F_1$ transition belongs to the magnetic dipole transition which scarcely changes the crystal field strength around the Eu^{3+} ions and this transition is independent of the symmetry and the site occupied by Eu^{3+} ions in the host [19]. While the transition of $^5D_0 \rightarrow ^7F_2$ belongs to a forced electric dipole transition and its intensity is very sensitive to the site symmetry of the Eu^{3+} ions. Thus, the ratio of $R = ^5D_0 \rightarrow ^7F_2 / ^5D_0 \rightarrow ^7F_1$ can measure the distortion from the inversion symmetry of the Eu^{3+} ion local environment [20]. Generally, phosphor having luminescence properties are strongly affected by concentration of rare earths materials. It is seems that in different type of synthesis method.

Normally, low doped activator gives weak luminescence but excess doping causes quenching of luminescence [21]. In our sample preparation the phosphor gives the maximum intensity of emission are observed at (Eu^{3+}) 0.5 mole % shown in Figure 5. The excitation spectrum is at 394 nm and it is properties of LED lighting and gives the emission in orange-red region and this phosphor may be good candidates for white LED lighting.

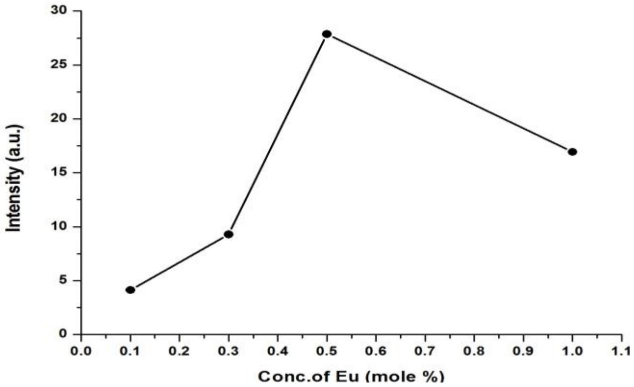

Figure 5. Variation in the PL intensity due to Eu^{3+} ion concentrations

Chromatic properties:

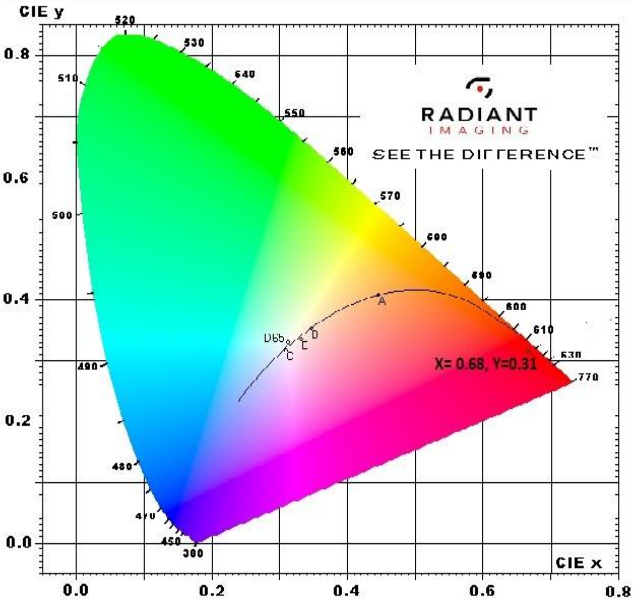

Figure 6. CIE chromatic diagram showing the coordinates

By using 1931 CIE chromatic colour coordinates are specified lighting that recognize human visual system uses three colours red, green and blue [22,23]. In this system the light sources are represented by (X, Y) coordinates and coloured are compared with1931 CIE diagram. The colour purity was compared to the 1931 CIE Standard Source C (illuminant Cs (0.3101, 0.3162)). The chromatic coordinates (x, y), was calculated using the colour calculator program radiant imaging [24]. In this article the coordinates of Eu^{3+} are doped $CaAl_3(PO_4)_3F_2$ Phosphor are located (X = 0.68,Y = 0.31) as shown in Figure 6 indicates that the colour properties of the phosphor powder prepared by combustion method is approaching those required for field emission displays. The dominant wavelength is the single monochromatic wavelength that appears to have the same colour as the light source. This result indicates that high colour purity of this $CaAl_3(PO_4)_3F_2$:Eu $^{3+}$ halophosphate phosphors because it is slightly near to the edge of the CIE diagram. Hence, such material may be an efficient photoluminescent material for solid-state lighting phosphors as a red component, and helpful in generating white light with a particular ratio of this phosphor.

IV. CONCLUSION

In present article, we synthesized $CaAl_3(PO_4)_3F_2$:Eu^{3+} halophosphate based phosphor by using combustion synthesis and characterized by XRD and spectrophotometer. We studied their photoluminescent properties and structure of this phosphor. Under the excitation around 394 nm $CaAl_3(PO_4)_3F_2$ phosphor shows orange red emission by doped Eu^{3+} and that phosphor could be promising good candidate for white light LED application.

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