

Spectroscopic Studies of Strong Red Emitting $\text{CaAl}_2\text{O}_4:\text{Eu}^{3+}$ Nano-phosphor for WLED's Applications Using Judd–Ofelt Theory

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Abstract

Eu^{3+} doped Calcium aluminate nanophosphor was fabricated via sonochemical route and characterized with scanning electron microscopy (SEM), X-ray diffraction (PXRD), photoluminescence (PL). PL excitation and emission spectrum were studied to explore the PL properties of $\text{CaAl}_2\text{O}_4:\text{Eu}^{3+}$ nanophosphor. The PL emission spectrum exhibit intense peaks at ~ 577, 588, 615, 654 and 702 nm, which were assigned to transitions of Eu^{3+} ions as $^5D_0 \rightarrow ^7F_1$, $^5D_0 \rightarrow ^7F_2$, $^5D_0 \rightarrow ^7F_3$ and $^5D_0 \rightarrow ^7F_4$ respectively. The chromaticity coordinates of the synthesised sample was projected to be (0.608, 0.393) and its corresponding correlated color temperature (CCT) was estimated to be ~ 1300 K, which is suitable for warm white light display applications. The Judd–Ofelt (J-O) intensity parameters and radiative characteristics such as radiative lifetime, transition probabilities, branching ratios and lifetimes for the excited states of Eu^{3+} ions were computed from the emission spectra using Judd–Ofelt (J-O) theory. From aforementioned results, $\text{CaAl}_2\text{O}_4:\text{Eu}^{3+}$ (5 mol %) nanophosphor can be regarded as a promising red phosphor, which is appropriate in solid state lighting and display devices using UV or blue chips.

Keywords: Bio-inspired; Sonochemical route; Photoluminescence; LED.

1.0 INTRODUCTION

Nanotechnology and Nanoscience together are showing many promising applications mainly in biology, information technology, nanoelectronics, medicinal field, etc., [1-3]. Therefore for future industrial revolution the blending of these two can be considered [4]. Alkaline earth aluminates with bright photoluminescence at visible region have attracted more interest in recent years [5]. Because of their important electronic, optical and structural properties. [6-8].

Traditional sources like incandescent and fluorescent lamps were having lower luminous efficacy and hence very sensitive to human eyes. Hence regular efforts were made by researchers to find efficient nanophosphors with unique properties [9 -12].

Calcium aluminate (CaAl_2O_4) develops more interest for the researchers due to its promising applications in the field of WLED'S, optical communications, biological labeling agents, low power laser therapy etc., [13 -15]. Further in developing a new way to find clear image of latent finger

prints(LFPs) the nanomaterials have been proposed with which we can identify most useful ridge details[16]. In general, photoluminescence observed in phosphors are assigned to the f to f or f to d transitions of lanthanides ions. Along to this, luminescence intensity depends on the the nature of the host lattice and site symmetry.

According to literature survey, no results are reported on the synthesis of CaAl_2O_4 via ultrasound sonication method hence in this work, $\text{CaAl}_2\text{O}_4:\text{Eu}^{3+}$ nanophosphor is synthesized by this method using lemon juice as a surfactant. The method is found to be cheap, fast, simple and safe. The synthesized nanophosphor is well characterized by Powder XRD, DRS, PL studies.

2. EXPERIMENTAL

$\text{CaAl}_2\text{O}_4:\text{Eu}^{3+}$ (5 mol %) nanophosphor was prepared by ultrasound assisted sonochemical route. The chemicals like analytical grade Aluminium nitrate [$\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (purity 99.9%)], Calcium nitrate [$\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$ (99.9%)], Europium oxide (Eu_2O_3) and lemon juice as a surfactant are taken in proper stoichiometric ratios. The metal nitrates

lemon juice of 30 ml and double distilled water was mixed with magnetic stirrer for 10 min to obtain a required clear solution. The resulting solution was kept for sonication by irradiating with ultrasound waves for 1 hr at 33 °C. The solution was then dried in an oven for a day to get a gel like sample, later annealed at 900 °C for 3 hr to receive the expected phase. The resultant nano powder was further examined by powder XRD, PL studies to know the phase formation and photoluminescence properties.

3. RESULTS AND DISCUSSION

3.1 PXRD

Fig.1 (a) shows the PXRD profiles of prepared CaAl₂O₄:Eu³⁺ (5 mol %) nanophosphor. The spectra reveal intense and narrow diffraction peaks as well as monoclinic phases is retained in the sample irrespective of the dopant (JCPDS 172155). This signifies that the dopant ions do not alter the phase structure significantly.

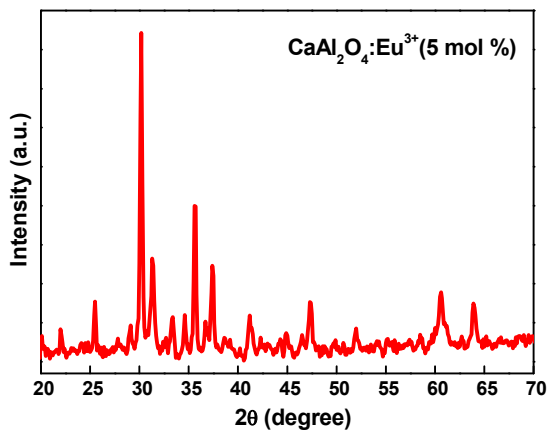


Fig.1(a): PXRD pattern of CaAl₂O₄:Eu³⁺(5 mol %) nanophosphor.

The Williamson - Hall's (W-H) plots of the prepared samples was depicted in Fig.1 (b). The average crystallite size (D) and strain existing in the nano samples was calculated by using the Debye Scherrer's and W-H relation [17];

$$D = \frac{0.9\lambda}{\beta \cos \theta} \dots\dots\dots (1)$$

$$\beta \cos \theta = \varepsilon (4 \sin \theta) + \frac{\lambda}{D} \dots\dots\dots (2)$$

where 'β'; FWHM of the peaks in radian, 'λ'; wavelength of X-ray (1.542 Å), 'ε'; strain present in the sample, 'D'; crystallite size and 'θ'; Bragg's angle. The estimated values of crystallite size are provided in Table 1.

3.2 PL

The photoluminescence spectrum of the sample is shown in Fig. 2 (a and b). The excitation spectra of nanophosphor recorded with emission at 615 nm. The

observed peaks at ~ 367, 393, and 463 nm are assigned as ⁷F₀ → ⁵G₃, ⁷F₀ → ⁵D₂ and ⁷F₀ → ⁵L₆ transitions of Eu³⁺ ions respectively. The spectra exhibits discrete features and all the emission peaks are obviously distinguishable. Hence, high potential aluminate phosphor CaAl₂O₄: Eu³⁺ synthesized by ultrasound assisted Sonochemical route showed visible emission at near visible excitation wavelength of light.

Table 1: Estimated crystallite size of CaAl₂O₄:Eu³⁺ (5 mol %) nanophosphor

CaAl ₂ O ₄ :Eu ³⁺ (mol %)	Crystallite size(nm)	
	D-S method	WH plot
5	31	33

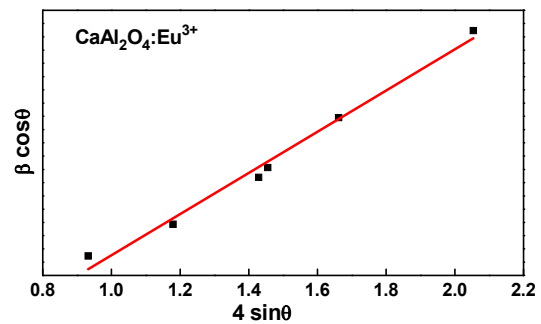


Fig.1(b) WH plot of CaAl₂O₄:Eu³⁺ (5 mol %) nanophosphor

The emission spectra of CaAl₂O₄:Eu³⁺ (5 mol %) nanophosphor recorded on excitation with 463 nm in the range of 550-700 nm . The spectra exhibits peaks at ~ 577, 588, 615, 654 and 702 nm are assigned as ⁵D₀ → ⁷F₀, ⁵D₀ → ⁷F₁, ⁵D₀ → ⁷F₂, ⁵D₀ → ⁷F₃ and ⁵D₀ → ⁷F₄ transitions of Eu³⁺ ions respectively. Among these, the peak centered at 615 nm was most prominent and is due to ⁵D₀ → ⁷F₂ transition.

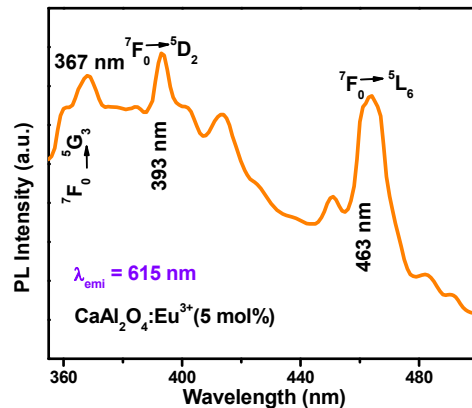


Fig.2 (a) : PL excitation spectra of CaAl₂O₄:Eu³⁺ (5 mol %) nanophosphor

The enhancement in the PL emission intensity is mostly due to crystallinity, reduced CIE optical quenching centers and energy transfer. The CIE plot for 5 mol % Eu³⁺ doped

CaAl₂O₄ nanophosphor is shown in Fig.2 (c). It was marked that the CIE chromaticity coordinates are located in the red region. To find the suitability of this orange red light, CCT is determined from coordinates of CIE Fig. 2(d). The correlated color temperature (CCT) gives color appearance of the light emitted by a source of light, relating its color to the light color from a reference source when heated to particular temperature. CCT was estimated by transforming the (x, y) coordinates of the light source to (U₀, V₀) by Planckian locus [18].

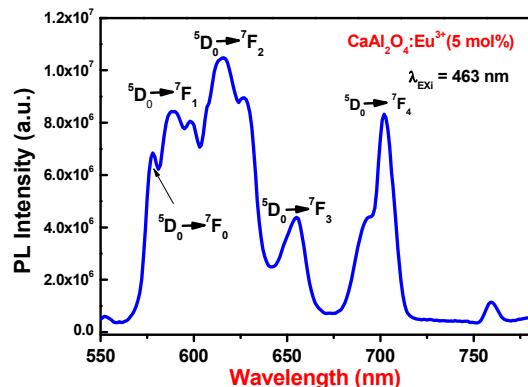


Fig.2 (b) : PL emission spectra of CaAl₂O₄:Eu³⁺ (5 mol %) nanophosphor

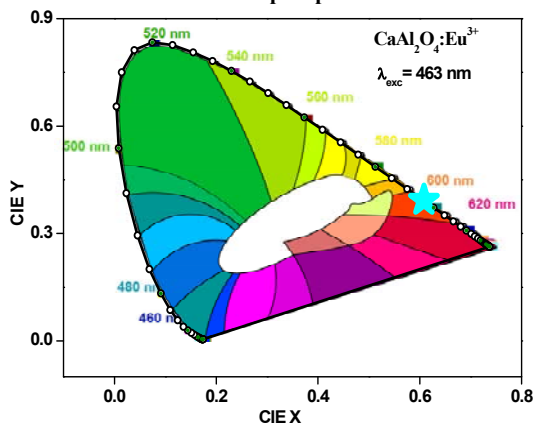


Fig.2 (c): CIE diagram of CaAl₂O₄:Eu³⁺ (5 mol %) nanophosphor

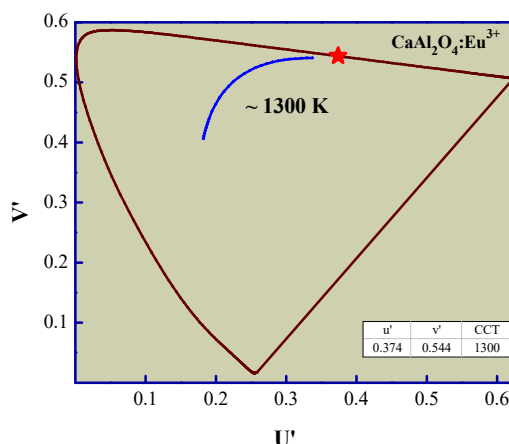


Fig.2 (d): CCT diagram of CaAl₂O₄:Eu³⁺ (5 mol %) nanophosphor

The energy band gap (E_g) of CaAl₂O₄: Eu³⁺ phosphor was estimated from UV-Vis reflectance spectra using Kubelka–Munk function. The photon energy ($h\nu$) and Kubelka–Munk function $F(R_\infty)$ were estimated by following equations [19].

$$h\nu = \frac{1240}{\lambda} \text{ ----- (3)}$$

$$F(R_\infty) = \frac{(1 - R_\infty)^2}{2R_\infty} \text{ ----- (4)}$$

where R_∞ ; coefficient of reflection of the sample, A ; the absorbance intensity of CaAl₂O₄: Eu³⁺ nanophosphor and λ ; the absorption wavelength. The observed band gap energy was found to be 5.3 eV (Fig 3).

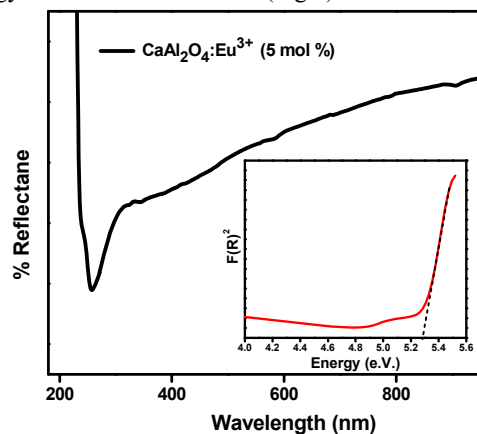


Fig.3. Diffusion reflectance spectra and inset optical band gap CaAl₂O₄:Eu³⁺ (5 mol %) nanophosphor

3.3 JUDD–OFELT THEORY

The Judd-Ofelt theory [20, 21] provides the intensities of transitions of rare earth ions, actinides and also provides transition branch ratios, radiative and nonradiative transition probabilities and lifetimes. Recently, the MathCad 14 program have been employed to find Ω_2

and Ω_4 experimental intensity parameters by measuring the areas under the emission curves and energy barycenters of the ${}^5D_0 \rightarrow {}^7F_2$ transitions using the magnetic dipole ${}^5D_0 \rightarrow {}^7F_1$ as one of the reference.

Table.2. Judd-Ofelt intensity parameters (Ω_2, Ω_4), Emission peak wavelengths (λ_p in nm), radiative transition probability (A_T), calculated radiative (τ_{rad}) lifetime and branching ratio (β_R) of Eu^{3+} doped nanophosphor ($\lambda_{ex} = 463$ nm).

CaAl ₂ O ₄ :Eu ³⁺ conc. (mol %)	Judd-Ofelt intensity parameters ($\times 10^{-20}$ cm ²)		Emission peak wavelength λ_p (nm)	A_T (s ⁻¹)	τ_{rad} (ms)	β_R
	Ω_2	Ω_4				
5	2.284	0.88	616.77	53.62	18.36	0.999

4 CONCLUSION

In the present work, the CaAl₂O₄: Eu³⁺ (5 mol %) nanophosphor was synthesized through ultrasound supported sonochemical route using lemon juice extract. The crystallite size of the prepared CaAl₂O₄:Eu³⁺ nanophosphor was estimated from W-H plots to be 33 nm which is equivalent to the size obtained via Debye Scherer's method. The enhancement in the PL emission intensity was mainly due to crystallinity, reduced optical quenching centers and energy transfer. The transition centered at 615 nm (${}^5D_0 \rightarrow {}^7F_2$) is found to be sensitive in nature resulting in a strong red emission. The spectroscopic parameters, including radiative transition probabilities, radiative lifetimes and branching ratios are determined according to the standard Judd-Ofelt theories. It is observed that CaAl₂O₄: Eu³⁺ phosphors have a long lifetime (τ) and the determined branching ratio of 0.999 suggests its suitability for display devices. CIE chromaticity coordinates are very close to NTSC standard value of red emission. Hence, the prepared nanophosphor was quite functional for WLED's and solid state lighting applications.

ACKNOWLEDGEMENT

The author B. S. Shashikala thanks Prof. C.N.R. Rao Centre for Advanced Materials, Tumakuru University for the instrumentation support to complete this work.

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