

**EFFECT OF UV IRRADIATION ON STABILITY OF Tb DOPED CaF₂ PHOSPHORS FOR ANTI-COUNTERFEITING APPLICATIONS**

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ABSTRACT

CaF₂:Tb³⁺ phosphor nanoparticles were synthesized via the co-precipitation method, yielding crystallites with an average size of 60-70 nm as confirmed by X-ray diffraction (XRD) analysis. The luminescence properties of the phosphor were characterized through photoluminescence (PL) spectroscopy, indicating dominant green emission upon excitation. This emission was further validated using CIE chromaticity coordinates, establishing its suitability for applications requiring green light emission. Stability analysis under UV irradiation indicated robust performance, demonstrating the phosphor's potential for long-term use in applications involving UV exposure. The synthesized CaF₂ phosphor holds capability for various technological applications including fluorescent lighting, security marking and radiation detection due to its stable and efficient luminescent behaviour.

Keywords: XRD, CIE Chromaticity, Co-precipitation, photoluminescence

I. Introduction:

Luminescent materials, renowned for their ability to emit light when excited by external energy sources, play a crucial role in various technological applications ranging from lighting and displays to biomedical imaging[1][2]. Among the diverse array of luminescent materials, phosphors stand out due to their efficient conversion of energy into visible light. These phosphors owe their luminescent properties predominantly to rare earth elements, which are integral components in their synthesis[3][4][5].

Calcium fluoride (CaF₂) serves as an excellent host material for rare earth dopants due to several advantageous properties. CaF₂ has a cubic crystal structure with a high symmetry, which allows for efficient incorporation of rare earth ions without significant distortion of the lattice. This structural stability contributes to maintaining the optical properties of the dopants, ensuring consistent and predictable emission characteristics. It exhibits a wide bandgap, which helps in preventing quenching effects and enhances the durability of luminescent materials under harsh environmental conditions. Moreover, the low phonon energy of CaF₂ (~400-500 cm⁻¹) minimizes non-radiative transitions, thereby promoting high luminescence efficiency of rare earth dopants embedded within its lattice[1][6]. These combined factors make CaF₂ a preferred host material for various luminescent applications, including phosphors for solid-state lighting, scintillators, and laser systems[7][8].

Tb³⁺ has been a well-known activator for some years now because of its multiple visible emissions in the green and blue range. These emissions originate from ⁵D₃-⁷F_J (J=6,5,4) and ⁵D₄-⁷F_J (J=6,5,4,3) transitions. A strong emission at 542 nm makes it a suitable dopant for green solid state lasers. When the distance between Tb³⁺ ions inside the host is sufficiently short, cross relaxation energy transfer takes place causing green to blue conversion via ⁵D₃ to ⁵D₄ energy exchange. Thus, concentration of Tb³⁺ ions becomes a vital parameter for the said phenomenon to occur.

The study of native point defects in CaF₂ involves investigating the intrinsic defects within the crystal lattice that affect its electronic and structural properties[8][9]. Native point defects such as vacancies interstitials and Frenkel pairs play important roles in determining the material's behaviour and characteristics. Researchers have employed techniques like first-principles calculations, defect modelling, and experimental spectroscopic methods to unravel the complex nature of native point

defects in CaF₂, aiming to enhance its efficiency, stability and reliability in practical applications such as radiation detectors, optical coatings and scintillators.

II. Materials and method

In the present work, Tb³⁺ doped CaF₂ nanoparticles have been synthesized using co-precipitation method. Shailesh *et al.* synthesized SrF₂ doped with Eu using wet chemical method[10]. All the materials used were of analytical grade and used as received. Ca(NO₃)₂.4H₂O and TbCl₃ were obtained from Sigma Aldrich. The quantities of materials used for synthesis is shown in the Table 1 below. The flowchart shown in fig 1 demonstrates the reaction method opted for nanoparticle synthesis.

Serial Number	Doping of Tb ³⁺ in CaF ₂ (mol %)	Quantity of Ca(NO ₃) ₂ (gram)	Quantity of TbCl ₃ (gram)
1.	0.01	2.3378	0.0265
2.	0.03	2.2906	0.0795
3.	0.05	2.2434	0.1326
4.	0.10	2.1253	0.2652

Table 1: Concentration of Tb³⁺ ions in CaF₂ Phosphor

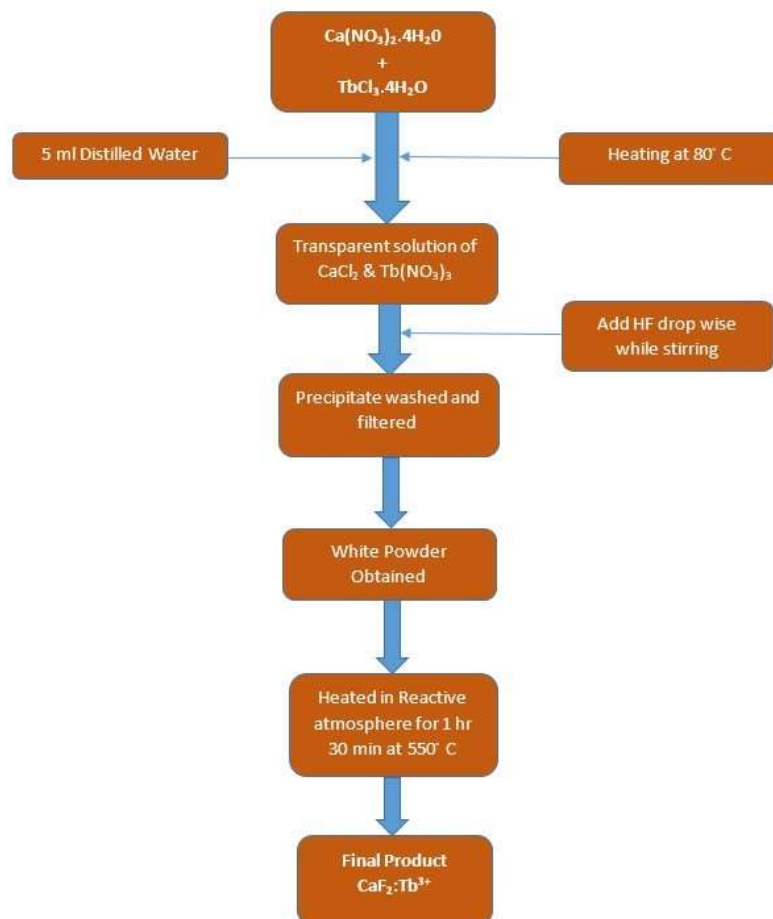


Fig 1: Synthesis method of CaF₂:Tb³⁺

III. Results and Discussion

XRD Analysis: A Rigaku Miniflex 600 diffractometer (Miniflex, Tokyo, Japan) using CuK α source ($\lambda = 1.5406 \text{ \AA}$) was used to obtain the XRD spectra of as prepared Tb doped CaF₂ nanophosphors. As shown in the fig 2 below, the cubic structure of CaF₂ was intact with no extra peaks obtained, thereby,

confirming the formation of nanophosphor. The patterns of samples with different concentrations show diffraction at 28.26, 46.945, 55.65, 68.6 and 75.67 which according to JCPDS 70-1469 correspond to (111), (220), (311), (400) and (331) planes respectively[11]. Ca^{2+} ions were substituted by Tb^{3+} ions and no extra peak was observed in the XRD pattern. The overall intensity was reduced with increase in the Tb concentration indicating deformation in the crystallinity. Scherrer's formula was used to calculate the crystallite size as shown below

$$D = \frac{k\lambda}{\beta \cos\theta}$$

Where, λ is the wavelength of $\text{CuK}\alpha$ (1.5406 Å), β is the FWHM and D is crystalline size[12]. The average crystallite size was found to be 68 nm for the sample doped with 0.10% Tb.

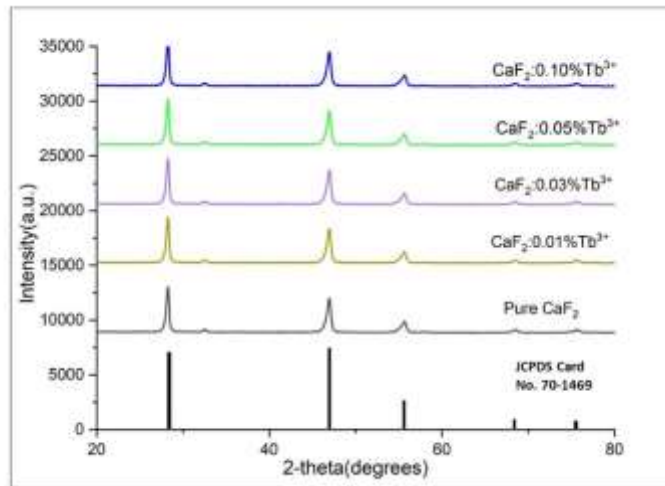


Fig 2: XRD pattern of $\text{CaF}_2:\text{Tb}^{3+}$ phosphor

Photoluminescence spectral analysis:

PL spectra of as prepared sample is taken using a Hitachi F7000 fluorescence spectrophotometer. The PL spectra of Tb^{3+} doped CaF_2 phosphors is shown in the fig 3. Multiple emissions (i.e. 488 nm, 541 nm, 581 nm and 620 nm) in the range of green region are observed when the sample is excited at 378 nm. These emissions may be attributed to $^5\text{D}_4-^7\text{F}_j$ ($J = 6, 5, 4, 3$) transitions. An increase in the emission intensity is observed with the increasing Tb^{3+} concentration. This may be attributed to the occurrence of cross relaxation phenomenon due to neighbour Tb^{3+} ions in the host lattice[9].

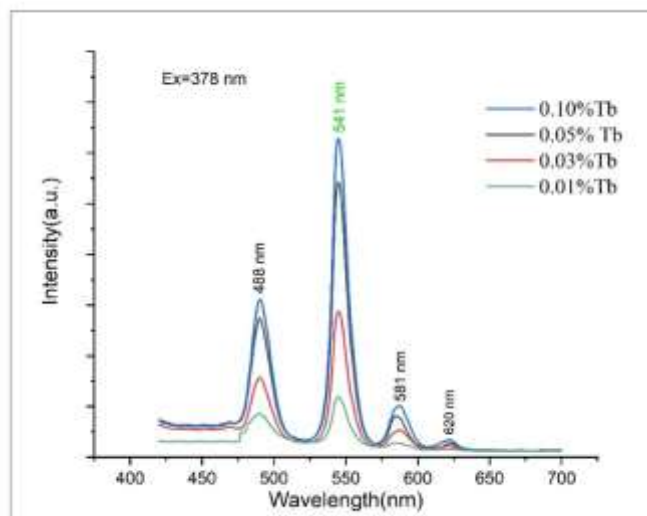


Fig 3: Emission spectra of Tb^{3+} doped CaF_2

The CIE coordinates of samples with 0.03, 0.05 and 0.10 at % Tb concentration were plotted according to 1931 CIE standards. A prominent green colour can be seen in the fig. 4. It is evident from the figure that the green emission intensity shifts towards standard green light coordinates ($x = 0.21, y = 0.71$) with an increase in doping concentration.

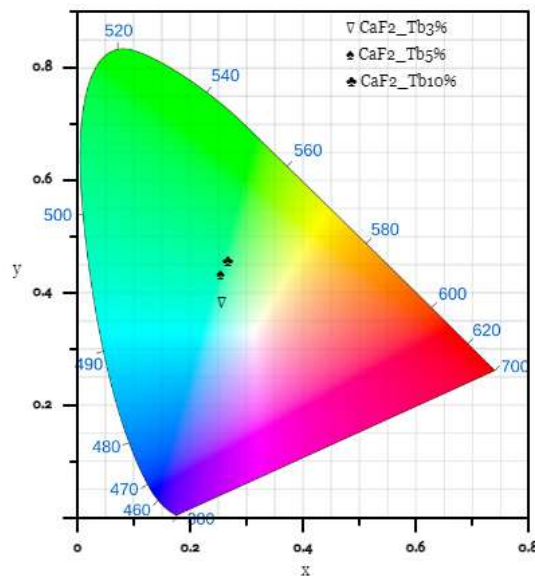


Fig 4: CIE chromaticity diagram for Tb³⁺(0.03,0.05,0.10 at %) Concentrations

Stability analysis:

The CaF₂ sample with 0.10% Tb³⁺ concentration was irradiated with 380 nm UV light for 5 hours and PL emission intensity was recorded as a function of time. The intensity variation in 541 nm peak was monitored every 15 minutes as shown in the Fig. 5 below. A slight degradation in the intensity was observed over time with no major change in the colour. It decreased slightly after ~2 hours which may be due to surface modifications because of environmental oxygen related adsorption. Mamykin *et al.* in 2011 in his work reported the degradation of CaF₂ phosphor after UV irradiation with a colour change of brown attributed to Tb³⁺ conversion to Tb⁴⁺ ions[13]. Godbole *et al.* reported no significant change for a short 5 min exposure to 258 nm UV light[14].

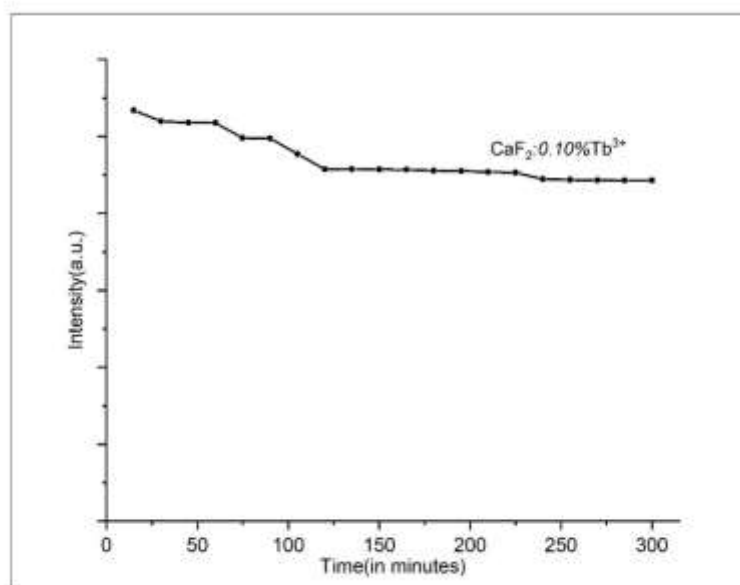


Fig. 5: PL stability Curve for 0.10% Tb³⁺

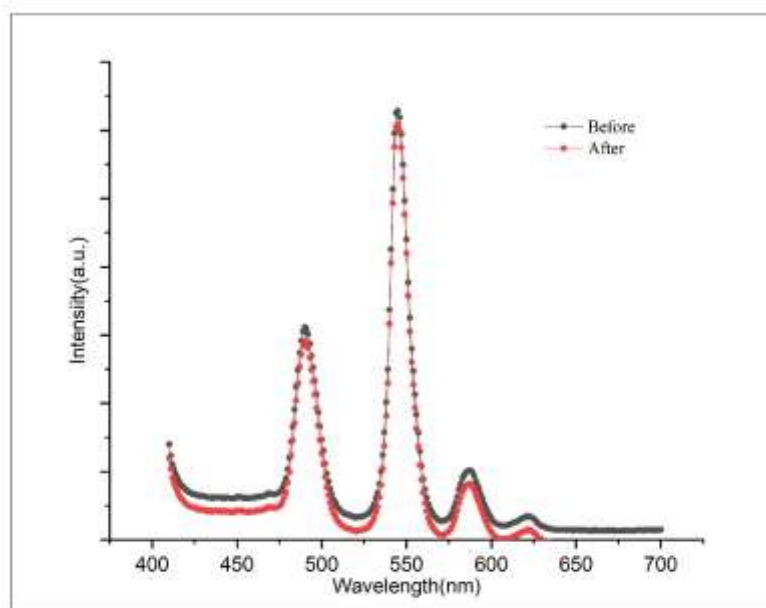


Fig 6: Emission spectra for 0.10% Tb^{3+} concentration

Fig. 6 shows the emission spectra of $CaF_2:Tb^{3+}$ (at 0.10%) sample recorded before and after irradiation. A marginal decrease in intensity is observed after irradiation with no notable colour change.

Conclusion

Tb^{3+} doped calcium fluoride (CaF_2) phosphor nanoparticles synthesized via co-precipitation exhibited promising luminescent properties. X-ray diffraction confirmed well-defined crystallites with an average size of 60-70 nm. Photoluminescence analysis demonstrated strong green emission, validated by CIE chromaticity coordinates, highlighting its efficacy in generating efficient green light. The phosphor showed wonderful stability under UV irradiation, essential for long-term performance in various applications such as ink preparation for security marking and anti-counterfeiting. This work recognizes CaF_2 as a robust candidate for future advancements in optoelectronic applications with potential optimizations to enhance optical performance.

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