

# White Light Emission Through Downconversion of Terbium and Europium Doped CeF<sub>3</sub> Nanophosphors

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**Abstract** CeF<sub>3</sub> nanophosphors have been extensively investigated in recent years for lighting and numerous bio-applications. Downconversion emissions in CeF<sub>3</sub>:Eu<sup>3+</sup>/Tb<sup>3+</sup> phosphors were studied with the objective of attaining a white light emitting composition, by means of a simple co-precipitation method. The material was characterized by X-ray Diffraction (XRD), Transmission Electron Microscopy (TEM), Fourier Transform Infrared Spectroscopy (FT-IR) and Photoluminescence (PL). Uniformly distributed nanoparticles were obtained with an average particle size range of 8–10 nm. Various studies were undertaken utilizing different doping concentrations and respective fluorescence studies were carried out to optimize dopant concentrations while achieving maximum luminescence intensity. From PL results, it was observed that the efficient energy transfers from the donor to the acceptor ions. Different concentrations of Tb<sup>3+</sup>, Eu<sup>3+</sup> were doped in order to achieve a white light emitting phosphor for UV-based Light Emitting Diodes (LEDs). The nanoparticles showed characteristic emission of respective dopants (Eu<sup>3+</sup>, Tb<sup>3+</sup>) when excited at the 4f→5d transition of Ce<sup>3+</sup>. The chromaticity coordinates for CeF<sub>3</sub> doped with Eu<sup>3+</sup> and Tb<sup>3+</sup> were calculated and an emission very close to white light was observed.

**Keywords** White light downconversion · Nanophosphors · LEDs · Rare earth · Cerium fluoride · Lanthanides · Bio-imaging

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## Introduction

In recent years, an increase in the trend is observed wherein white-light emitting diodes (W-LEDs) replace the conventional incandescent and fluorescent lamps [1]; and also as backlighting in full color liquid crystal displays (LCDs) owing to their longer operational lifetimes, lower energy consumptions, higher material stability, and environment friendly characteristics [2, 3].

The operation of LEDs is based upon the spontaneous emission of light by semiconductors; due to the radiative recombination of excess electrons and holes, produced via the injection of current. Subsequently, LEDs are therefore not constrained by crucial variables that exist in traditional and fluorescent lighting devices. Thus, it is well established that LED light sources have a predominant proficiency, lifetime, and reliability; making them more energy efficient and environment friendly with lower thermal radiations and free of toxic mercury. Phosphor-based WLEDs are classified by the categories of transmitting materials; for example, inorganic phosphors, organic phosphors, organic–inorganic hybrid phosphors, and colloidal semiconducting nanocrystals or quantum dots (QDs). LEDs share a similarity in its principle of operation with organic light emitting diode (OLED) or polymer light-emitting diode (PLED), but its application is restricted by the effect of circumstance on organics. At present, the application of LEDs has been extended from signal indicators to automobile light, traffic light, street lighting, landscape decoration, and backlight of liquid crystal display (LCD) for TV sets, computers and mobile telephones [4].

There are two major approaches in realizing WLEDs. The first method entails WLED fabrication by means of simply mixing three colors of red, green, and blue LEDs [5]. However, the emission power exponentially decays with increase in temperature, which leads to substantial changes in color

stability. The second method involves coating of a mono colored LED (preferably blue) with downconversion phosphors resulting in white light production. To this day, a method more popular than the aforementioned phosphor-based fabrication of high intensity WLEDs is yet to be discovered. The popularity of the method can be accounted to the advantages of easy control of colors and reduced manufacturing costs the process entails [4, 5].

Rare earth (RE) doped nanoparticles have been synthesized that make use of  $\text{Ce}^{3+}$  sensitization to obtain red, green, and blue emissions via single UV excitation wavelength [6]. Through this paper, a method for obtaining highly tailorable white light emissions by means of single nanoparticle excitation utilizing a single UV wavelength is described. These emissions, obtained through the development of nanoparticles using co-precipitation method, permit energy transfer control between the lanthanide dopant ions.

$\text{CeF}_3$ , selected as the host material for the active nanoparticles due to its well-known properties as an optical material; enables low vibrational energies, high thermal and chemical stability, and high solubility for optically active RE dopants. Such a UV-excited phosphor would be of interest for white LED applications in accordance to the color fixation capability of the LED provided by it during particle growth. Further, the color should be stable regardless of the thickness or concentration of the phosphor conversion layer. Subsequently, thicker conversion layers could be used to maximize UV light conversion [7].

$\text{Ce}^{3+}$  exhibits a very high UV absorption coefficient originated from the allowed electric dipole  $4f \rightarrow 5d$  transition [8]. Taking  $\text{Ce}^{3+}$  as the sensitizer, the efficient energy transfer from  $\text{Ce}^{3+}$  to the other RE ions would result in strong RE emissions [9].  $\text{CeF}_3$  has gained high research interest by virtue of its technological significance as an inorganic scintillating crystal [10–12] due to its properties (high density, fast response time, and high resistance to radiation). The efficient absorption and energy transfer by the host (to activator) is another advantage of  $\text{CeF}_3$  nanophosphors [13].

This paper outlines  $\text{CeF}_3:\text{Eu}^{3+}, \text{Tb}^{3+}$  nanophosphor synthesis by a co-precipitation method. The downconversion properties were studied systematically.

## Experimental

### Reagents

All reagents used for synthesis were purchased from Sigma Aldrich. High purity precursors, lanthanide salts ( $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ ,  $\text{Eu}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ ,  $\text{Tb}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ ) and ammonium fluoride were used as received without further purification. Oleic acid used was purchased from Merck.

## Synthesis of Doped Cerium Fluoride Nanoparticles

$\text{CeF}_3$  nanophosphors doped with various RE activator ions were synthesized by a co-precipitation route. In a typical synthesis 20 ml ethanol; in which total of 0.02 M of  $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  and the corresponding concentration of the RE nitrate and oleic acid (0.002 M) were dissolved. Ammonium fluoride (0.06 M) was dissolved in 80 ml distilled water and heated to  $70^\circ\text{C}$ . Both solutions were mixed and stirred for 10 min. The nanoparticles were precipitated out by adding ethanol, washed several times by centrifugation, and dried under ambient conditions.

### Characterization

X-ray diffraction (XRD) measurements for the synthesized samples were carried out on a Philips powder diffractometer (PW3040/60 X'pert pro), operating with  $\text{Cu-K}\alpha$  radiation ( $\lambda=0.15405\text{ nm}$ ) with a scan rate of  $0.02\text{ s}^{-1}$  in the scattering angular range ( $2\theta$ ) of  $20^\circ$  to  $90^\circ$ . TEM micrographs were recorded on a JOEL JEM-2100 F. The samples were dispersed in ethanol solution and then deposited on the carbon copper grids for TEM/SAED studies. Photoluminescence (PL) was carried out on a Horiba Jobin-Yvon FluroLog-3 model. The FTIR spectra of the solid sample were recorded using a Bomem MB102 FTIR (model 610) in the mid IR region ( $4000\text{--}400\text{ cm}^{-1}$ ) equipped with a DTGS detector having a resolution of  $4\text{ cm}^{-1}$ . For this purpose about 100 mg dry KBr was mixed with 1 mg of the sample. It was ground and pressed into a transparent pellet at  $5\text{ t cm}^{-2}$ . These pellets were used for IR spectral measurements.

## Results and Discussions

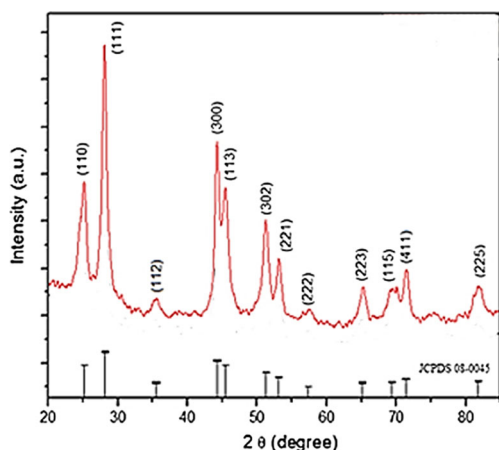
Prepared  $\text{CeF}_3$  nanophosphors were characterized by XRD, TEM, PL spectroscopy and FTIR.

### X-ray Diffraction

The phase structures of the nanophosphors were investigated by XRD. Figure 1 shows XRD Patterns of  $\text{CeF}_3:\text{Eu}, \text{Tb}$  and the standard data for  $\text{CeF}_3$  (JCPDS) as well. The results of XRD indicate that the samples synthesized are well crystallized, and the pattern is consistent with the hexagonal phase structure known from the bulk  $\text{CeF}_3$  crystal (JCPDS: 08–0045). Additionally, no other peak can be found in the patterns, revealing that there is no impurity in the products.

### TEM

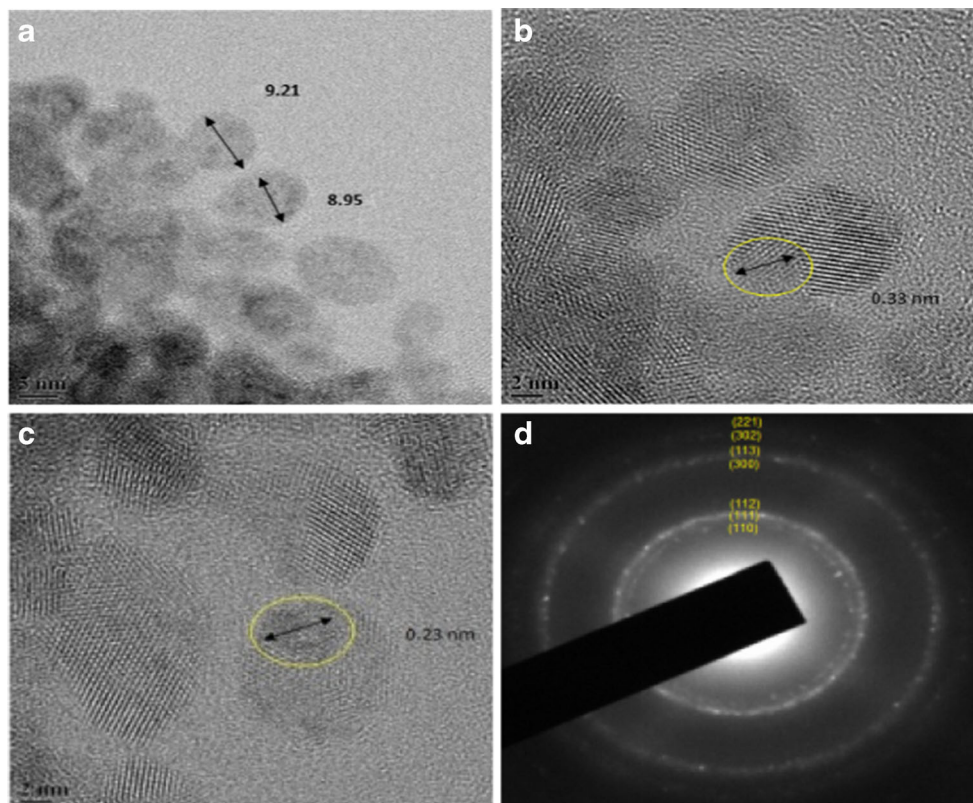
The TEM image (Fig. 2) was recorded for a particular white light composition. TEM images of scales: 5 and



**Fig. 1** XRD patterns of  $\text{CeF}_3$ : Eu, Tb and the standard  $\text{CeF}_3$  file obtained from JCPDS: 08–0045

2 nm depict the particle size (8–10 nm) and shape (spherical). In Fig. 2c (scale 2 nm) change in the surface morphology depicted that the dopant successfully had become embedded into the lattice. The Selected Area Electron Diffraction (SAED) pattern indicated that the nanoparticles are polycrystalline in nature. Figure 2d shows seven diffuse diffraction rings, which can be indexed as the (110), (111), (112), (300), (113), (302) and (221) phases of the hexagonal  $\text{CeF}_3$  starting from the inner to the outer ring, which is in coherence with the XRD patterns.

**Fig. 2** TEM images of  $\text{CeF}_3$  codoped at different scales along with SAED. **a** scale: 5 nm; **b** and **c** scale: 2 nm; and **d** SAED

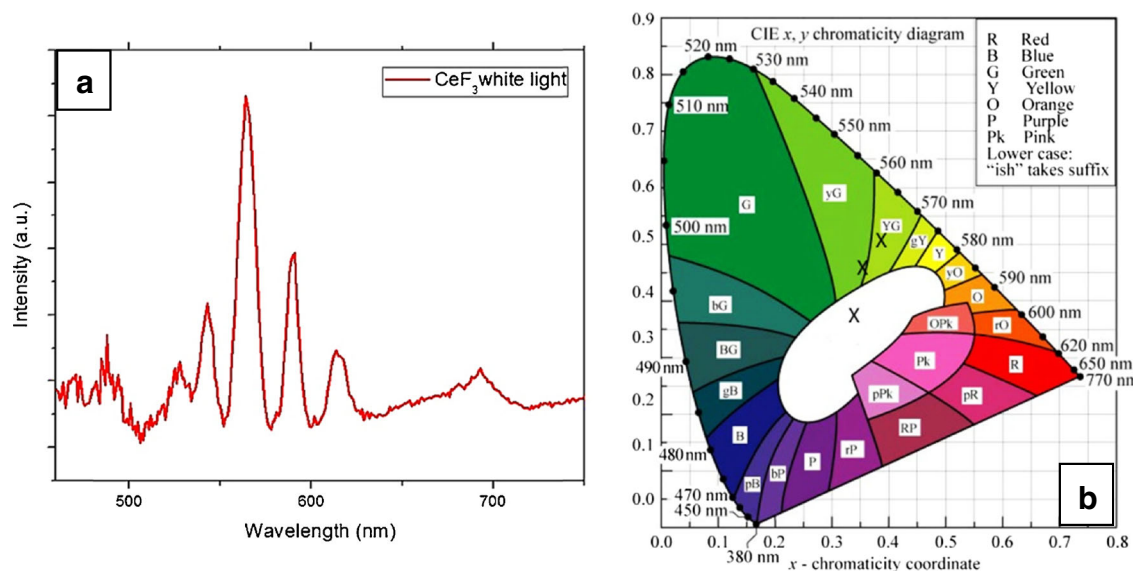


## Photoluminescence (PL) Studies

Detailed PL studies were carried out on  $\text{CeF}_3$ :  $\text{Eu}^{3+}$ ,  $\text{Tb}^{3+}$ . The emission spectra (Fig. 3a) was monitored from 450 to 765 nm spectrum by exciting the sample at 273 nm. The Commission Internationale de l'Eclairage 1931 chromaticity (CIE) diagram was used to reflect the true color of luminescence. Respective CIE calculation was performed for the sample. The chromaticity coordinates of  $\text{CeF}_3$ : 20 %Eu, 0.1 %Tb particles were calculated to be about  $x=0.34$ ,  $y=0.36$ , which is very close to the white light. The concentration of Eu was changed from 10 to 30 %. The chromaticity coordinates of various compositions of  $\text{CeF}_3$ : Eu, Tb is described in the table (Fig. 3c).

## FTIR Studies

To explore the surface of the nanoparticles, FT-IR studies were performed on the doped  $\text{CeF}_3$  nanophosphors. The prominent peaks were observed at 2854.01 and 2925.17  $\text{cm}^{-1}$  in the C–H stretching region (4000–1300  $\text{cm}^{-1}$ ) attributable to the symmetric and asymmetric C–H stretches, respectively in the FT-IR spectrum recorded (Fig. 4). The weak absorption at 2956.7  $\text{cm}^{-1}$  results from the asymmetric stretching of the terminal  $-\text{CH}_3$  group of the alkyl chain. The peak at 3005.5  $\text{cm}^{-1}$  indicates that C–



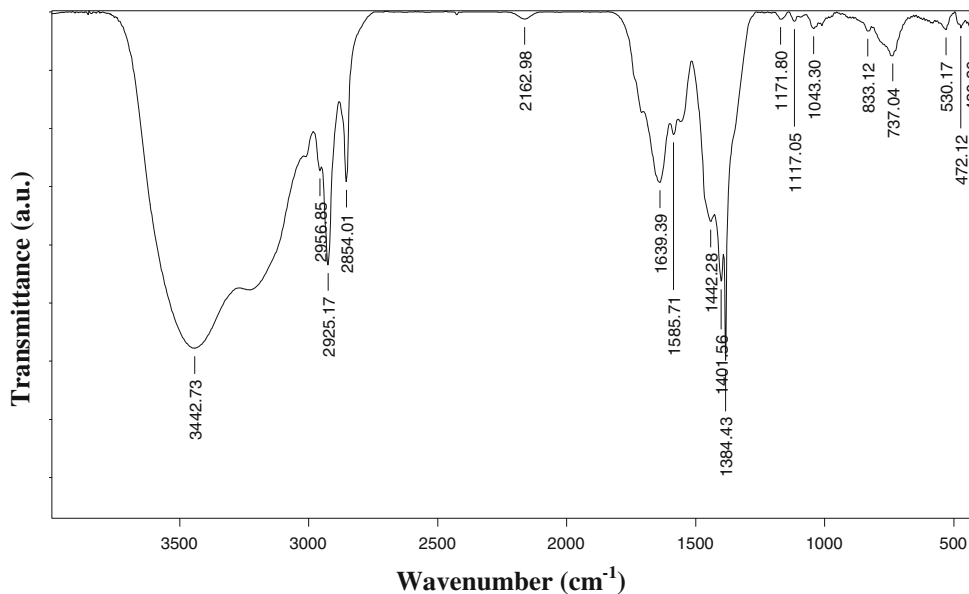
Compositions	X co-ordinate	Y co-ordinate
<b>c</b> CeF <sub>3</sub> :10%Eu,0.1%Tb	0.39	0.50
CeF <sub>3</sub> :20%Eu,0.1%Tb	0.34	0.36
CeF <sub>3</sub> :30%Eu,0.1%Tb	0.40	0.45

**Fig. 3** a PL emission of CeF<sub>3</sub>: Eu, Tb obtained after exciting the sample at 273 nm; b CIE chromaticity diagram CeF<sub>3</sub>:20 %Eu,0.1 %Tb; c Table depicting x and y CIE co-ordinates for various compositions

H stretching is involved. Meanwhile, in the fingerprint region (below 1300 cm<sup>-1</sup>), the absorption at 721 cm<sup>-1</sup> clearly proves the existence of the (CH<sub>2</sub>)<sub>n</sub> (n>4) alkyl chains. A strong absorption was observed at 1639 cm<sup>-1</sup>, which is attributed to the stretching vibrations of the CO group. But two characteristic bands centered at 1444 and 1585 cm<sup>-1</sup> were observed, which can be associated with the -COO<sub>2</sub> asymmetric and symmetric stretching

vibrations of carboxylate anions bound to the CeF<sub>3</sub> surface. Thus it indicates the presence of oleic acid in the sample. It can be implied that the oleic acid present in the sample may affect the overall luminescence intensity of the nanophosphors therefore it is paramount that optimization be performed to achieve proper concentrations of oleic acid. Also, proper washing shall ensure better results due to the removal of excess oleic acid.

**Fig. 4** FT-IR spectra of CeF<sub>3</sub>





## Conclusions

CeF<sub>3</sub> nanoparticles were successfully synthesized by simple co-precipitation route. Spherical nanoparticles were obtained in the size range of 8–10 nm; confirmed by TEM. White light was emitted by the CeF<sub>3</sub> nanoparticles with 20 % doping concentration of Eu and 0.1 % doping concentration of Tb. The CIE coordinates of the CeF<sub>3</sub> nanoparticles was found to be close to that of broad day light. These CeF<sub>3</sub> nanophosphors have the potential to be developed into solid state lighting devices with probable potential applications in solid state lasers, telecommunications, opto-electronics, and bio-medical devices and/or applications.

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