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# Solid state white light emitting systems based on CeF<sub>3</sub>: RE<sup>3+</sup> nanoparticles and their composites with polymers

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#### ABSTRACT

A series of doped CeF<sub>3</sub>:  $RE^{3+}$  ( $RE^{3+}$ :  $Tb^{3+}$ ,  $Eu^{3+}$  and  $Dy^{3+}$ ) nanoparticles were synthesized, with the aim of obtaining a white light emitting composition, by a simple polyol route at 160 °C and characterized by X-ray diffraction (XRD), high resolution transmission electron microscopy (HR-TEM), Fourier transform infrared spectroscopy (FT-IR) and photoluminescence. Uniformly distributed and highly water-dispersible rectangular nanoparticles (length ~15-20 nm, breadth ~5-10 nm) were obtained. The steady state and time resolved luminescence studies confirmed efficient energy transfer from the host to activator ions. Lifetime studies revealed that optimum luminescence is observed for  $2.5 \text{ mol}\% \text{ Dy}^{3+}$  and 7.5 mol% Tb<sup>3+</sup>. The energy transfer efficiencies (Ce<sup>3+</sup> to activators) were found to be 89% for CeF<sub>3</sub>: Tb<sup>3+</sup> (7.5 mol%) nanoparticles and 60% for CeF<sub>3</sub>: Dy<sup>3+</sup> (2.5 mol%) nanoparticles. Different concentrations of Tb<sup>3+</sup>, Eu<sup>3+</sup> and Dy<sup>3+</sup> were doped to achieve a white light emitting phosphor for UV-based LEDs (light emitting diodes). Finally CeF<sub>3</sub>, triply doped with 2.0 mol<sup>7</sup> Tb<sup>3+</sup>, 4.5 mol<sup>8</sup> Eu<sup>3+</sup> and 3.5 mol<sup>8</sup> Dy<sup>3+</sup>, was found to have impressive chromaticity co-ordinates, close to broad day light. The colloidal solutions of doped CeF<sub>3</sub> nanoparticles emitted bright green (Tb<sup>3+</sup>), blue (Dy<sup>3+</sup>) and white (triply doped) luminescence upon host excitation. Composites of poly methyl methacrylate (PMMA) and poly vinyl alcohol (PVA) were made with CeF<sub>3</sub>: 5.0 mol% Tb<sup>3+</sup>, CeF<sub>3</sub>: 5.0 mol% Dy<sup>3+</sup> and triply doped white light emitting composition. The CeF<sub>3</sub>/PMMA (PVA) nanocomposite films, so obtained, are highly transparent (in the visible spectral range) and exhibit strong photoluminescence upon UV excitation.

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#### 1. Introduction

Solid state lighting (SSL) refers commonly to the light emitted by solid-state electroluminescence, as opposed to incandescent bulbs or fluorescent tubes. Compared to incandescent lighting, SSL creates visible light with reduced heat generation or parasitic energy dissipation. It is contemplated as an efficient lighting technology that offers a lot of potential to save energy. Solid state lighting utilizes LEDs or light emitting diodes. One way to create white light source is to use multiple LED chips, each emitting a different wavelength in close proximity to create the broad white light spectrum. The second method, phosphor-converted LEDs (pcLEDs) uses a single short wavelength LED (usually blue or ultraviolet) in combination with a phosphor, which absorbs a portion of the blue light and emits a broader spectrum of white light. In view of this, a lot of research has been directed towards synthesizing good quality phosphors which can efficiently absorb UV light given by LED to emit desired colors. Lanthanide ions (or rare-earth ions) are important in this context as their luminescence is characterized by sharp lines and high efficiency. That is why, in the past decade, the syntheses and optical characterization of rare-earth ions doped nanoparticles have aroused material scientists' interest. Most research work basically focuses on rare-earth oxide [1,2], phosphates [3–6], and borates. Inorganic fluorides nanocrystals doped with rare-earth ions have shown unique luminescence properties and hence are good candidates as host materials with correspondingly useful applications in optical telecommunication, lasers, new optoelectronic devices as well as in diagnostics and biological labels [3-10]. The fluoride lattice provides for the high coordination number for the doped rare-earth ions and the high ionicity of the rare-earth to fluorine bond results in a very wide band gap, low vibrational energies and low probability of inter-configurational transitions. This results in long lifetimes of their excited states and high luminescence quantum yields. Therefore, recently the investigation of nanosized rare-earth fluorides has increased manifold [11-14].

Among the rare-earth fluorides, cerium fluoride ( $CeF_3$ ) has been attracting increasing attention by virtue of its technological importance as an inorganic scintillating crystal [15–17] because of its high density, fast response, and high-radiation resistance. Efficient

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absorption and energy transfer by host (to activator) is another advantage associated with using CeF<sub>3</sub>. It is also an important fluorescent host material owing to its low vibrational energies and the subsequent minimization of the quenching of the excited state of the rare-earth ions [18]. Hence, many methods to produce bulk CeF<sub>3</sub> have been reported like the Czochralski (CZ) technique [17,19–21], Bridgeman method [22–24], MOCVD [25] and molecular beam epitaxy [26]. There have been several reports on synthesis of CeF<sub>3</sub> nanoparticles by various wet chemical techniques [18,27– 33].

In context of solid state phosphor, an important characteristic is the color which can be described in terms of *x* and *y* coordinates, also called Chromaticity coordinates or CIE co-ordinates (Commission Internationale d'Eclairage) which are derived from the color matching functions or the tristimulus response functions. Most "white" LEDs in production today are modified blue LEDs coated with a yellow emitting phosphor (YAG: Ce<sup>3+</sup>) [34,35]. It would be a worthwhile to synthesize a material which is a white light emitting solid phosphor and wherein all the RGB (red, green, blue) components are contained within the same host matrix as this option would have better wavelength coverage over the visible range. Recently, studies have been done wherein the CeF<sub>3</sub> nanocrystals embedded glass ceramics were fabricated with doped RE ions incorporated into the nanocrystals which emitted an intense white light under UV excitation [36].

If incorporated in a suitable polymer matrix, nanoparticles of such rare-earth fluorides can be used in a variety of applications ranging from biological to optoelectronics. The introduction of inorganic nanoparticles into a polymer matrix has proved to be an effective method to improve the performance of polymer materials and bring about novel properties in them [37,38]. Two promising polymer matrices in this regards are poly methyl methacrylate (PMMA) and poly vinyl alcohol (PVA). While PMMA/rare-earth fluoride nanocomposites can be used to develop high-grade optoelectronic devices such as light emitting diodes (LEDs), security labeling [39] lasers [40], and displays [41], PVA based nanocomposites can be used in biological imaging and other diagnostic applications. Chai et al. reported synthesis of nanocomposites of  $CeF_3$  nanoparticles [42].

In the present work, we report a facile one pot synthesis of redispersible CeF<sub>3</sub> nanoparticles doped with various visible emitting ions in different concentrations to get the optimum concentration of individual activator. With the aim of developing solid state phosphor consisting of all red, blue and green component which can be made to emit white light by single wavelength UV excitation, attempts were made to dope different activators in CeF<sub>3</sub> and optimize their concentrations to finally get a white light emitter for applications in solid state lighting devices. To demonstrate the suitability of these nanoparticles for use in devices and in biological and optoelectronic applications, attempts have also been made to develop PMMA and PVA based transparent nanocomposites of a few representative compositions, retaining the luminescence characteristics of original nanoparticles.

#### 2. Materials and methods

#### 2.1. Materials

High purity (99.9%) cerium nitrate [Ce(NO<sub>3</sub>)<sub>3</sub>6H<sub>2</sub>O], europium nitrate [Eu(NO<sub>3</sub>)<sub>3</sub>6H<sub>2</sub>O], terbium nitrate [Tb(NO<sub>3</sub>)<sub>3</sub>4H<sub>2</sub>O], dysprosium nitrate, [Dy(NO<sub>3</sub>)<sub>3</sub>5H<sub>2</sub>O] and sodium fluoride [NaF] were obtained from commercial sources (Aldrich). All the chemicals were used as obtained, without further purification. PVA (MW 125,000, LR) in powdered form, was procured from Prabhat Chemicals, India

and average molecular weight PMMA was procured from a local supplier. Acetone used was of AR grade (purity > 99%).

#### 2.2. Characterization techniques

The starting materials and all the nominal compositions were characterized by powder-XRD on a Philips instrument, operating with Cu K $\alpha$  radiation ( $\lambda$  = 1.5406 Å) with a scan rate of 0.02°/s in the scattering angular range  $(2\theta)$  of 10–70°. Silicon was used as an external standard for correction due to instrumental line broadening. The XRD patterns were analyzed by comparing them with the reported ones. The average crystallite size was calculated from the diffraction line width based on Scherrer's relation. High resolution TEM micrographs were recorded on JEOL 2000FX. The samples were dispersed in methanol solution and then deposited on the carbon coated copper grids for TEM/SAED studies. Photoluminescence (PL) and lifetime investigations were carried out on an Edinburgh F-LSP920. A microsecond 100 W Xe flash lamp was used as the excitation source. Ce<sup>3+</sup> life time values have been measured using a nano second hydrogen flash lamp operating at 40 K H<sub>2</sub>. The decay is deconvulated after taking instrumental response into consideration. The CIE color coordinates (x, y) were calculated with the equidistant wavelength method based on the photoluminescence emission spectra. The FT-IR spectra of the solid samples were recorded in KBr using a Bomem MB102 FT-IR (model 610) in the mid IR region (4000–400  $\text{cm}^{-1}$ ) equipped with a DTGS detector having a resolution of 4 cm<sup>-1</sup>. For this purpose about 200 mg of dry KBr was mixed with 10 mg of the sample, ground and pressed into a transparent, thin pellet at 5 tons/cm<sup>2</sup>. These pellets were used for IR spectral measurements.

## 2.3. Synthesis of cerium fluoride nano particles doped with $RE^{3+}$ ( $RE^{3+}$ : $Tb^{3+}$ , $Eu^{3+}$ and $Dy^{3+}$ ) and their polymer nanocomposites

In a typical procedure, stoichiometric amount of Ce(NO<sub>3</sub>)<sub>3</sub>6H<sub>2</sub>O and desired RE(NO<sub>3</sub>)<sub>3</sub>6H<sub>2</sub>O were dissolved in 25 ml of ethylene glycol and heated to 100 °C. At this temperature, NaF dissolved in 25 ml of ethylene glycol (also at same temperature) was added drop wise to the reaction mixture. The temperature was raised to 160 °C and maintained for 2 h. The precipitate obtained was washed several times with acetone and ethanol and dried under ambient conditions. Various nominal compositions of  $Ce_x RE_{1-x}F_3$  (0.025  $\leq$  $x \le 0.10$ , RE<sup>3+</sup> = Tb<sup>3+</sup> and Dy<sup>3+</sup>) were prepared to investigate the effect of concentration of dopant on the optical properties of the doped cerium fluoride. Triply-doped samples ( $Tb^{3+}$ ,  $Dy^{3+}$  and  $Eu^{3+}$ ) of CeF<sub>3</sub> were also prepared by the similar route. Nanocomposites these nanoparticles were prepared by sonicationof assisted dispersion followed by solvent casting. Suitable amount of nanoparticle filler was dispersed in 5.0% polymer solution to yield polymer nanocomposites containing 1.0% nanoparticulate filler (w/w). The samples were casted in glass discs and dried at 40 °C.

#### 3. Result and discussion

#### 3.1. Sample characterization

The as-prepared products obtained after polyol synthesis were characterized by powder-XRD. The XRD pattern for undoped CeF<sub>3</sub> matches well with the reported data for CeF<sub>3</sub> (PCPDF file No. 72-1436) and it possesses hexagonal symmetry (SG: P6<sub>3</sub>22). The patterns indicates that the sample is well crystallized and the lattice parameters were calculated to be a = 7.1136 Å, c = 7.2611 Å, which are in good agreement with that reported in the literature for bulk CeF<sub>3</sub>. The XRD patterns for doped CeF<sub>3</sub>: RE<sup>3+</sup> (Tb<sup>+</sup>, Dy<sup>3+</sup>) are similar to undoped CeF<sub>3</sub> thus showing that the parent structure is retained

in the doped samples as well. The diffraction peaks in the XRD pattern are broadened due to smaller crystallite size which was estimated using Scherrer's equation. The strongest peak (1 1 1), was used to calculate the average crystallite size (*D*) of the samples which was found to be ~15 nm for all the samples. The XRD patterns for undoped CeF<sub>3</sub> and representative doped CeF<sub>3</sub> nanoparticles are shown in Fig. 1A.

High resolution-TEM data were recorded on a few representative compositions. Uniformly distributed rectangular nanoparticles with length  $\sim$ 15–20 nm and breadth  $\sim$ 5–10 nm are observed. The particles are uniformly distributed and fairly regular in shape and size. The size of the nanocrystals is found to be in the range of 15–20 nm which is in good agreement with that determined from XRD line broadening. HR-TEM micrographs show distinct fringes indicating high crystallinity of the samples. The rings observed in SAED pattern indicate that the nanoparticles are polycrystalline in nature. The observed rings can be completely indexed with respect to hexagonal phase of CeF<sub>3</sub>. A representative HR-TEM as well as SAED on triply-doped compositions CeF<sub>3</sub>: 2.0 mol% Tb<sup>3+</sup>, 3.5 mol% Dy<sup>3+</sup>, 4.5 mol% Eu<sup>3+</sup> is shown in Fig. 1B.



**Fig. 1.** (A) X-ray diffraction patterns of (a) CeF<sub>3</sub>; (b) CeF<sub>3</sub>: 5.0 mol% Tb<sup>3+</sup>; (c) CeF<sub>3</sub>: 5.0 mol% Dy<sup>3+</sup>; (B) HR-TEM pattern of CeF<sub>3</sub>: 2.5 mol% Dy<sup>3+</sup>; (C) FT-IR pattern of CeF<sub>3</sub>: 2.5 mol% Dy<sup>3+</sup>.

The nanoparticles were also characterized by FT-IR spectroscopy to confirm the stabilization of ligands on the surface of nanoparticles. Fig. 1C shows the IR spectra of as-prepared CeF<sub>3</sub>: 2.5 mol $^{3+}$  nanoparticles. There is a broad hump peaking at 3397 cm<sup>-1</sup> which is due to O-H stretching vibrations. The small band at 2945 cm<sup>-1</sup> and 2883 cm<sup>-1</sup> correspond to asymmetric and symmetric stretching of -CH<sub>2</sub> group. The band at 1600 cm<sup>-1</sup> is due to -OH bending. Similarly, the small bands at 1450 cm<sup>-1</sup> and  $780 \text{ cm}^{-1}$  represent scissoring and rocking motion of  $-\text{CH}_2$  group [43]. The band at 1085 cm<sup>-1</sup> can be assigned to C–O–H stretching. The band at 2356 cm<sup>-1</sup> is due to the absorption of CO<sub>2</sub> from atmosphere on the surface of nanoparticles. All these indicate the presence of ethylene glycol molecules as stabilizers on the nanoparticles' surface. The presence of ligands (like ethylene glycol) on the surface of nanoparticles plays a vital role in making them dispersible in polar solvents like water and methanol. Good dispersibility is an important criterion that aids ease of fabrication and also facilitate the use of nanoparticles for biological assays and imaging.

Representative atomic force microscopic (AFM) image for the polymer sample incorporated with nanoparticles is shown in Fig. 1D. The image mainly consists of irregular shaped small islands (white regions) distributed on a smooth surface. The small islands are characteristic of the nanoparticles whereas the smooth surface corresponds to the polymer matrix. Some of the nanoparticles are also found to be aggregated. The approximate height of these nanoparticles (white regions) are found to be in the range of 10–15 nm. Based on the AFM studies, it is inferred that the nanoparticles are uniformly distributed in the polymer matrix.

#### 3.2. Photoluminescence and decay studies

#### 3.2.1. $CeF_3$ : $xDy^{3+}$ (x = 2.5, 5.0, 7.5, 10.0 mol%)

Detailed photoluminescence studies were carried out on CeF<sub>3</sub> doped with varying concentrations of Dy<sup>3+</sup> ion. The excitation and emission spectra of CeF<sub>3</sub>: xmol% Dy<sup>3+</sup> samples (x = 2.5, 5.0, 7.5, 10.0) are shown in Fig. 2.

Characteristic Dy<sup>3+</sup> emission profile at 478 nm and 571 nm are observed for all the nominal compositions. Left side inset shows the excitation spectrum of the sample monitored at  $\lambda_{em}$  = 571 nm. A broad hump peaking at 252 nm was observed which can be assigned to the host  $Ce^{3+}$  transition (4f-5d). In the emission spectrum recorded at host excitation (252 nm), intense peaks are observed at 478 nm and 571 nm which correspond to  ${}^{4}F_{9/2} \rightarrow {}^{6}H_{15/2}$ (blue–green color) and  ${}^{4}F_{9/2} \rightarrow {}^{6}H_{13/2}$  (yellow color) of Dy<sup>3+</sup>, respectively. The absence of the direct excitation peak of Dy<sup>3+</sup> (at 355 nm) in the excitation spectrum as well as the appearance of  $Dy^{3+}$  emission profile at host excitation, indicate that the energy transfer from host lattice (Ce<sup>3+</sup>) is the major mode of Dy<sup>3+</sup> excitation. Decay studies showed a bi-exponential decay. This could be attributed to the Dy<sup>3+</sup> present in the different surroundings (presumably in the bulk and on the surface) which will give different decay lifetimes with the faster decaying component being the one present on the surface due to faster quenching of the excited state. However, the faster decaying component is present in minority. Fig. 3 shows the decay curves corresponding to the  ${}^{4}F_{9/2}$  level of Dy<sup>3+</sup> in the CeF<sub>3</sub> nanoparticles containing different concentrations of  $Dy^{3+}$ . The corresponding lifetime values for  ${}^{4}F_{9/2}$  level of  $Dy^{3+}$  are also shown in Fig. 3.

There is a continuous decrease in lifetime values with increase in Dy<sup>3+</sup> concentrations, which can be explained based on concentration quenching due to cross-relaxation among Dy<sup>3+</sup> ions. Hence, it can be inferred from abovementioned results that among the compositions synthesized, CeF<sub>3</sub>: 2.5 mol% Dy<sup>3+</sup> will have best luminescence properties.

Due to the strong absorption in the wavelength range of 200 and 300 nm resulting from the allowed 4f–5d transition of Ce<sup>3+</sup>, the doped CeF<sub>3</sub> nanocrystals show intense emission upon short-wavelength UV irradiation. The right hand inset of Fig. 2 gives photographs of bright visible luminescence in aqueous suspensions as well as powders of the Dy<sup>3+</sup> doped CeF<sub>3</sub> nanocrystals, irradiated with UV light. As can be seen from the abovementioned figure, the nanoparticles have very good dispersibility in the water and the colloidal solutions of these doped CeF<sub>3</sub> nanoparticles give bright luminescence.



**Fig. 2.** Emission spectrum of CeF<sub>3</sub>:  $xDy^{3+}$  nanoparticles (x = 2.5, 5.0, 7.5, 10.0 mol%) obtained after exciting the samples at 252 nm. Left hand inset shows the excitation spectrum;  $\lambda_{em} = 571$  nm. Right hand inset shows the bright blue luminescence of the nanoparticles in aqueous medium and as powder on glass slide. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)



**Fig. 3.** Decay curves corresponding to the  ${}^{4}F_{9/2}$  level of Dy<sup>3+</sup> in GdF<sub>3</sub>: xDy<sup>3+</sup> nanoparticles with x = (a) 2.5, (b) 5.0, (c) 7.5, (d) 10.0 mol%. Samples were excited at 252 nm and emission monitored at 571 nm.



**Fig. 4.** Emission spectrum of CeF<sub>3</sub>: xTb<sup>3+</sup> nanoparticles (x = 2.5, 5.0, 7.5, 10.0 mol%) obtained after exciting the samples at 252 nm. Left hand inset shows the excitation spectrum;  $\lambda_{em} = 542$  nm. Right hand inset shows the bright green luminescence of the nanoparticles in aqueous medium and as powder on glass slide. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

#### 3.2.2. $CeF_3$ : $xTb^{3+}$ (x = 2.5, 5.0, 7.5, 10.0 mol%)

Fig. 4 shows the emission spectrum for CeF<sub>3</sub>: xmol% Tb<sup>3+</sup> (x = 2.5, 5.0, 7.5, 10.0) nanoparticles, obtained after exciting the samples at host excitation and the inset shows the excitation spectrum at 542 nm (characteristic Tb<sup>3+</sup> emission). The right hand inset shows the bright green luminescence emitted by CeF<sub>3</sub>: Tb<sup>3+</sup> nanoparticles in water and in powdered form, on UV irradiation.

Very poor emission spectra were obtained from these samples on direct excitation of the Tb<sup>3+</sup> ions at 350 nm. However, as also in the case of Dy<sup>3+</sup>, sharp emission peaks at 487 nm, 542 nm, 580 nm and 620 nm ( ${}^{5}D_{4} \rightarrow {}^{7}F_{I}$  of Tb<sup>3+</sup>) are observed on exciting at 254 nm (host excitation). Here also, energy transfer seems to be the major mode for activator (here Tb<sup>3+</sup>) excitation. In order to study the effect of concentration on luminescence of CeF<sub>3</sub>: Tb<sup>3+</sup> nanoparticles, and determine the optimum concentration of activator Tb<sup>3+</sup> ion, photoluminescence studies were performed on CeF<sub>3</sub> doped with varying  $Tb^{3+}$  concentrations (viz. 2.5, 5.0, 7.5, 10.0 mol%). Fig. 5 shows the decay curves corresponding to the <sup>5</sup>D<sub>4</sub> level of Tb<sup>3+</sup> in nanoparticles containing different concentrations of Tb<sup>3+</sup>. Lifetime values for <sup>5</sup>D<sub>4</sub> level of Tb<sup>3+</sup> in 2.5, 5.0, 7.5, 10.0 mol% Tb<sup>3+</sup> doped CeF<sub>3</sub> are also given in Fig. 5 which reveal that the lifetime value is maximum for 7.5 mol% Tb<sup>3+</sup>. Long lifetime values indicate that the non-radiative decays are less and these nanophosphors will have better photoluminescence quantum yields.

Based on the above discussion it is clear that there exists strong energy transfer between  $Ce^{3+}$  (donor) to  $Tb^{3+}$  or  $Dy^{3+}$  ions (acceptor) and that is responsible for the bright luminescence from the nanoparticles on UV excitation. In order to quantify the energy transfer, lifetime for the lowest excited state of  $Ce^{3+}$ , both in presence and absence of the acceptor has been measured and the corresponding decay curves are shown in Fig. 6.

Undoped CeF<sub>3</sub> nanoparticles showed a bi-exponential decay with life time values around 14.999 ns. For the representative doped nanoparticles of CeF<sub>3</sub>: Tb<sup>3+</sup>(7.5 mol%) and CeF<sub>3</sub>: Dy<sup>3+</sup>(2.5 mol%) also, the decay curves are biexponential, however the lifetime values are significantly low compared to the undoped sample, as can be seen from Fig. 6. As the concentrations of Tb<sup>3+</sup>



**Fig. 5.** Decay curves corresponding to the  ${}^{5}D_{4}$  level of Dy<sup>3+</sup> in GdF<sub>3</sub>:  $xDy^{3+}$  nanoparticles with x = (a) 2.5, (b) 5.0, (c) 7.5, (d) 10.0 mol%. Samples were excited at 252 nm and emission monitored at 542 nm.



**Fig. 6.** Decay plots for CeF<sub>3</sub>, CeF<sub>3</sub>: Tb<sup>3+</sup> (7.5 mol%) and CeF<sub>3</sub>: Dy<sup>3+</sup> (7.5 mol%) monitoring Ce<sup>3+</sup> emission with instrumental response.

and Dy<sup>3+</sup> ions (acceptors) are relatively lower compared to Ce<sup>3+</sup> (donor), it is necessary to know the efficiency of energy transfer between the donor and acceptor. This been calculated based on the equation  $\eta = 1 - I_d/I_{d0} = 1 - \tau_d/\tau_{d0}$ , where  $I_d$ ,  $I_{d0}$  and  $\tau_d$ ,  $\tau_{d0}$  are the intensity of emission and excited state life time of the donor in presence and absence of the acceptor respectively. In a powder pattern it is quite possible that the intensities of the peaks may not be true representation of the luminescence efficiency, hence the lifetime values are used for calculating the energy transfer efficiency. The value is found to be 89% for CeF<sub>3</sub>: Tb<sup>3+</sup> (7.5 mol%) nano-particles and 60% for CeF<sub>3</sub>: Dy<sup>3+</sup> (2.5 mol%) nanoparticles compared to CeF<sub>3</sub>: Tb<sup>3+</sup> (7.5 mol%) nanoparticles can be attributed to the lower quenching concentration of Dy<sup>3+</sup> (less than 2.5 mol%) compared to Tb<sup>3+</sup> (around 7.5 mol%) ions. Schematic diagram for the energy transfer process from  $Ce^{3+}$  to  $Tb^{3+}$  and  $Dy^{3+}$  ions is shown in Fig. 7.

#### 3.2.3. Triply-doped CeF<sub>3</sub>: $RE^{3+}$ ( $RE^{3+}$ : $Dy^{3+}$ , $Tb^{3+}$ , $Eu^{3+}$ )

With the aim of synthesizing white light emitting solid state phosphor, CeF<sub>3</sub> lattice was doped with all the three activators  $Tb^{3+}$  (green),  $Dy^{3+}$  (blue) and  $Eu^{3+}$  (red). The concentrations of the three activators were then optimized to get a mixed emission corresponding to broad day light. To start with, CeF<sub>3</sub> doped with 2.5 mol% of all the three activators was synthesized and studied. The sample thus prepared was characterized as before, by powder-XRD confirming the monophasic nature of the product with hexagonal structure. For the photoluminescence studies, the sample was excited at host excitation and the emission spectrum was found to consist of emission peaks corresponding to all the activators. To evaluate the material performance on color luminescent emission, CIE chromaticity coordinates (x, y) were determined. Any color or hue, can be represented in terms of in terms of its *x* and y coordinates, also called Chromaticity co-ordinates or CIE co-ordinates. They are derived from the color matching functions or the tristimulus response functions. Since monochromatic radiation is a boundary of color-mixing, the chromaticity coordinate diagram can be constructed with *x* and *v*, the advantage of which is that we have a set of normalized values which can be used to compare colors having different intensity values. The diagram in which any one of the three-chromaticity coordinates is plotted against any other is called a chromaticity diagram. It is known that CIE co-ordinates of an ideal white light region of the chromaticity diagram lie in the range x = 0.28-0.35, y = 0.30-0.37. The CIE coordinates were calculated for the nominal composition CeF<sub>3</sub>: 2.5 mol% Tb<sup>3+</sup>, 2.5 mol% Eu<sup>3+</sup>, 2.5 mol% Dy<sup>3+</sup> (A) and are found to be x = 0.33, y = 0.40. The composition was lying majorly in green region and therefore to increase the red and blue components, nominal composition with dopant concentrations as 2.5 mol% Tb<sup>3+</sup>, 3.5 mol%  $Dy^{3+}$  and 3.5 mol%  $Eu^{3+}$  (B) was synthesized which led to

further improvement of the CIE co-ordinates. Another nominal composition CeF<sub>3</sub>: 2.0 mol% Tb<sup>3+</sup>, 3.5 mol% Dy<sup>3+</sup> and 3.5 mol%  $Eu^{3+}$  (C) was also tried and finally with CeF<sub>3</sub>: 2.0 mol% Tb<sup>3+</sup>, 3.5 mol%  $Dy^{3+}$  and 4.5 mol%  $Eu^{3+}$  (D), CIE co-ordinates very close to broad day light could be observed. The CIE co-ordinates for this particular composition are found to be x = 0.33, y = 0.36. The emission spectra of this white light emitting triply-doped compositions  $(\lambda_{ex} = 253 \text{ nm})$  are shown in Fig. 8. It can be clearly seen that the emission peaks due to all the three activators span almost the entire visible range. The chromaticity diagram depicting the CIE coordinates of all these triply-doped compositions is shown in Fig. 9. Energy dispersive X-rays (EDX) analysis was done on white light emitting composition CeF<sub>3</sub>: 2.0 mol% Tb<sup>3+</sup>, 3.5 mol% Dy<sup>3+</sup>, 4.5 mol% Eu<sup>3+</sup>. Other than the presence of Ce, Eu, Dy, Tb and F, the EDX results show the presence of C and O, which are there due to the presence of ethylene glycol molecules adsorbed on nanoparticles' surface, as was also confirmed by IR studies. Since ethylene glycol molecules are randomly adsorbed at on the surface, so for calculating the amounts of various species present, the amount of C and O were ignored. The nominal Composition was CeF<sub>3</sub>: 2.0 mol% Tb<sup>3+</sup>, 3.5 mol% Dy<sup>3+</sup>, 4.5 mol% Eu<sup>3+</sup> and the EDX results gave the composition as; CeF<sub>3</sub>: 2.8 mol% Tb<sup>3+</sup>, 3.8 mol% Dy<sup>3+</sup>, 4.0 mol% Eu<sup>3+</sup>

Composition D lies in the white light region of the spectrum as is also shown by the chromaticity diagram. The inset in Fig. 9 shows white light emission from the colloidal solution of nanoparticles of sample D. Lifetimes of the three activators were also determined in various triply-doped compositions and are listed in Table 1. It is seen that on co-doping the activators, the lifetime values of Tb<sup>3+</sup> have decreased whereas that of Dy<sup>3+</sup> increase. CeF<sub>3</sub> singly doped with 2.5 mol% Eu<sup>3+</sup> and 1 mol% Eu<sup>3+</sup> were

CeF<sub>3</sub> singly doped with 2.5 mol% Eu<sup>3+</sup> and 1 mol% Eu<sup>3+</sup> were synthesized and subjected to luminescence studies. The excitation and emission spectra of CeF<sub>3</sub>: 1.0 mol% Eu<sup>3+</sup> are shown in Fig. 10 wherein no Eu<sup>3+</sup> emission corresponding to host excitation is observed.



**Fig. 7.** Schematic diagram showing the energy transfer between the host  $CeF_3$  and  $Tb^{3+}/Dy^{3+}$  ions. Relevant levels of  $Dy^{3+}$  are only shown. Dotted lines are non-radiative transitions.



**Fig. 8.** Emission spectrum of white light emitting composition CeF<sub>3</sub>: 2.0 mol% Tb<sup>3+</sup>, 3.5 mol% Dy<sup>3+</sup>, 4.5 mol% Eu<sup>3+</sup>;  $\lambda_{ex}$ : 253 nm.



**Fig. 9.** Representation of CIE co-ordinates on Chromaticity diagram for all the triply doped composition; (A) CeF<sub>3</sub>: 2.5 mol%  $\text{Tb}^{3+}$ , 2.5 mol%  $\text{Dy}^{3+}$ , 2.5 mol%  $\text{Eu}^{3+}$ , (B) CeF<sub>3</sub>: 2.5 mol%  $\text{Tb}^{3+}$ , 3.5 mol%  $\text{Dy}^{3+}$ , 3.5 mol%  $\text{Eu}^{3+}$ , (C) CeF<sub>3</sub>: 2.0 mol%  $\text{Tb}^{3+}$ , 3.5 mol%  $\text{Dy}^{3+}$ , 3.5 mol%  $\text{Dy}^{3+}$ , 3.5 mol%  $\text{Dy}^{3+}$ , 4.5 mol%  $\text{Eu}^{3+}$ .

It is noteworthy that  $Eu^{3+}$  doped as a single dopant in CeF<sub>3</sub> lattice did not show any characteristic  $Eu^{3+}$  peaks in the emission spectrum. It has been postulated that in presence of Ce<sup>3+</sup>, quenching of emission in Ce<sup>3+</sup> and Eu<sup>3+</sup> co-doped systems occur. The Ce<sup>3+</sup>



**Fig. 10.** Emission spectrum of CeF<sub>3</sub>: 1.0 mol% Eu<sup>3+</sup>;  $\lambda_{ex}$  = 254 nm. Inset shows the excitation spectrum;  $\lambda_{em}$  = 612 nm. Schematics of energy quenching in presence of codoping of Ce<sup>3+</sup> and Eu<sup>3+</sup> is given in the inset.

electron excited to the lowest 5d state can jump to Eu<sup>3+</sup> when the unoccupied Eu<sup>2+</sup> ground state is located at a lower energy than the occupied lowest Ce<sup>3+</sup> 5d excited state. After the jump, Eu<sup>2+</sup> and  $Ce^{4+}$  are formed. The  $Eu^{2+}$  electron can jump back to  $Ce^{4+}$  if the unoccupied Ce<sup>3+</sup> ground state is located below the occupied Eu<sup>2+</sup> ground state. The original situation is restored without emission of a photon [44]. The schematics of this process is given in inset of Fig. 10. However, in the co-doped compositions, Eu<sup>3+</sup> gives distinct emission peaks. If it is to be assumed that Eu<sup>3+</sup> is excited by charge transfer due to Eu-O bonds of Eu<sup>3+</sup> ions present on the surface of nanoparticles, then in that case Eu<sup>3+</sup> emission should have been observed in singly-doped  $CeF_3$ :  $Eu^{3+}$  also. Further, the redox reaction between Ce<sup>3+</sup> and Eu<sup>3+</sup> is also ruled out since Eu<sup>3+</sup> emission is observed in co-doped compositions. A closer look at lifetime values in triply-doped compositions and their comparison with those of singly doped composition hint at energy transfer from Tb<sup>3+</sup> to Eu<sup>3+</sup>. It is known that doping Tb<sup>3+</sup> along with Eu<sup>3+</sup> improves the luminescence from Eu<sup>3+</sup> due to the energy transfer from Tb<sup>3+</sup> to Eu<sup>3+</sup> ions. Also, in the co-doped compositions, emission spectra recorded at 349 nm and 379 nm (which are intra f-f transitions for Tb<sup>3+</sup>), showed emission peaks characteristics of both Eu<sup>3+</sup> and Tb<sup>3+</sup> which further reiterates an energy transfer operating from Tb<sup>3+</sup> to Eu<sup>3+</sup>. The emission spectrum recorded at 349 nm is shown in Fig. 11. In fact the peak due to Dy<sup>3+</sup> also appears which indicates that energy transfer might be occurring from Tb<sup>3+</sup> to Dy<sup>3+</sup> as well. This also explains the increase in lifetime of Dy<sup>3+</sup>in co-doped samples as compared to that in singly doped samples. Even the excitation spectra recorded at the emission wavelength 618 nm (Eu<sup>3+</sup> emission) showed peaks at 315 nm, 349 nm and 379 nm which, as mentioned above, are characteristic direct excitation of Tb<sup>3+</sup> intra f-f transitions.

Table 1

 $Life time \ values \ (in \ ms) \ for \ ^4F_{9/2}, \ ^5D_4 \ and \ ^5D_0 \ levels \ of \ Dy^{3+}, \ Tb^{3+} \ and \ Eu^{3+} \ respectively \ in \ the \ triply-doped \ CeF_3 \ samples.$ 

Compositions	Lifetime values (in ms)		
	$\lambda_{\rm em}$ = 488 nm ( <sup>4</sup> F <sub>9/2</sub> of Dy <sup>3+</sup> )	$\lambda_{\rm em}$ = 543 nm ( <sup>5</sup> D <sub>4</sub> of Tb <sup>3+</sup> )	$\lambda_{\rm em} = 618 \text{ nm} ({}^{5}\text{D}_{0} \text{ of } \text{Eu}^{3+})$
CeF <sub>3</sub> : 2.5 mol% Tb <sup>3+</sup> , 2.5 mol% Eu <sup>3+</sup> , 2.5 mol% Dy <sup>3+</sup> CeF <sub>3</sub> : 2.5 mol% Tb <sup>3+</sup> , 3.5 mol% Eu <sup>3+</sup> , 3.5 mol% Dy <sup>3+</sup> CeF <sub>3</sub> : 2.0 mol% Tb <sup>3+</sup> , 3.5 mol% Eu <sup>3+</sup> , 3.5 mol% Dy <sup>3+</sup> CeF <sub>3</sub> : 2.0 mol% Tb <sup>3+</sup> , 3.5 mol% Eu <sup>3+</sup> , 4.5 mol% Dy <sup>3+</sup>	4.329 (88.9%) 0.542 (11.1%) 3.229 (87.9%) 0.227 (12.0%) 1.425 (100%) 2.710 (81.4%) 0.299 (18.5%)	4.816 (88.7%) 0.869 (11.2%) 4.404 (88.4%) 0.548 (11.5%) 4.327 (89.4%) 0.626 (10.5%) 4.187 (87.0%) 0.798 (12.9%)	5.245 (94.1%) 0.479 (5.8%) 4.605 (90.3%) 0.294 (9.6%) 4.628 (88.9%) 0.313 (11.0%) 4.294 (93.8%) 0.265 (6.1%)



Fig. 11. Emission spectrum of triply-doped CeF\_3: 2.0 mol% Tb^{3+}, 3.5 mol% Dy^{3+}, 4.5 mol% Eu^{3+};  $\lambda_{ex}$ : 349 nm.

#### 3.3. CeF<sub>3</sub>: RE<sup>3+</sup> nanoparticles-polymer composites

Of late, nanoparticle-polymer composites have attracted a great deal of interest for applications involving nanoparticles. For applications in light sources, apart from the fast response and phosphor, it is of utmost importance that phase separation of nanoparticles can be avoided which leads to the turbid polymer product because of scatter. Hence it is vital to get a transparent nanoparticles-polymer composite product. To test above mentioned nanoparticles on this criteria, green emitter CeF<sub>3</sub>: 5.0 mol% Tb<sup>3+</sup>, blue emitter CeF<sub>3</sub>: 2.5 mol% Dy<sup>3+</sup> and white light emitter CeF<sub>3</sub>: 2.0 mol% Tb<sup>3+</sup>, 3.5 mol% Dy<sup>3+</sup>, 4.5 mol% Eu<sup>3+</sup> were embedded in poly methyl methacrylate (PMMA) and poly vinyl alcohol (PVA). It was found that nanoparticles were dispersible in the polymers and highly transparent films of these nanoparticles-polymer composite were ob-



**Fig. 12.** Representative emission spectra of (a) blank polymer PMMA without nanoparticles; (b) CeF<sub>3</sub>: 5.0 mol% Tb<sup>3+</sup>/PMMA nanocomposite;  $\lambda_{ex}$ : 254 nm. Inset shows the excitation spectrum;  $\lambda_{em}$  = 542 nm.



**Fig. 13.** (a) Picture of unirradiated transparent polymer film embedded with CeF<sub>3</sub>: 5.0 mol% Tb<sup>3+</sup>. (b) (1) Bright green and blue emission from CeF<sub>3</sub>: 5 mol% Tb<sup>3+</sup>/ PMMA, (2) CeF<sub>3</sub>: 5 mol% Tb<sup>3+</sup>/PVA and (3) CeF<sub>3</sub>: 2.5 mol% Dy<sup>3+</sup>/PMMA on UV irradiation. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

tained. The photoluminescence spectra were recorded on these films and it was observed that they gave good emission spectra with very sharp peaks at host excitation, indicating efficient energy transfer. The representative emission spectra of the blank polymer PMMA without nanoparticles and that of CeF<sub>3</sub>: 5.0 mol% Tb<sup>3+</sup>/ PMMA nanocomposite at  $\lambda_{ex}$  = 254 nm are shown in Fig. 12. It is clearly seen that polymer does not have any emission of its own, as expected. The representative transparent polymer film containing CeF<sub>3</sub>: 5.0 mol% Tb<sup>3+</sup> is shown in Fig. 13a. Fig. 13b shows the CeF<sub>3</sub>: 5.0 mol% Tb<sup>3+</sup>/PMMA (1), CeF<sub>3</sub>: 5.0 mol% Tb<sup>3+</sup>/PVA (2) and CeF<sub>3</sub>: 2.5% Dy<sup>3+</sup> (3) films emitting bright colors on irradiation with UV light.

Previously doped CeF<sub>3</sub> nanoparticles prepared by ultrasonication were reported by the group [31] but these were not water dispersible. Water-dispersibility is desirable for various applications like bioapplications. Furthermore, the present work is a more detailed study on doped CeF<sub>3</sub> nanoparticles involving study of their composites with plolymers like polymethyl methacrylate (PMMA) and polyvinyl alcohol (PVA). There is also a detailed study and calculation of energy transfer from host to dopants (Tb<sup>3+</sup> and Dy<sup>3+</sup>).

#### 4. Conclusions

Rare earth doped CeF<sub>3</sub> nanoparticles were successfully synthesized by a convenient one pot polyol synthesis employing ethylene glycol as a solvent. Highly water dispersible, rectangular nanoparticles having size in the range of 15-20 nm were obtained as confirmed by XRD and TEM. Bright green luminescence was given by CeF<sub>3</sub>: Tb<sup>3+</sup> and blue luminescence by CeF<sub>3</sub>: Dy<sup>3+</sup> nanoparticles upon host (CeF<sub>3</sub>) excitation. No energy transfer was observed in the case of singly doped Eu<sup>3+</sup> in CeF<sub>3</sub> though codoping with Dy<sup>3+</sup> and Tb<sup>3+</sup> gave good Eu<sup>3+</sup> emission peaks. After trying with different concentration of various activators by trial and error, triply doped composition consisting of 2.0 mol% Tb<sup>3+</sup>, 3.5 mol% Dy<sup>3+</sup> and 4.5 mol% Eu<sup>3+</sup> in CeF<sub>3</sub> was found to give CIE co-ordinates very close to broad daylight. PVA and PMMA based transparent nanocomposites of some representative green, blue and white light emitting compositions were synthesized and these films were shown to emit bright luminescence upon UV irradiation. Energy transfer could be retained in these films. Hence this shows that these phosphors have the potential to be developed into solid state lighting devices.

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