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Biocompatible luminescent Ce³⁺-sensitized SrF₂:Tb³⁺ for anticounterfeiting and forensic fingerprint detection

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Ce³⁺-sensitized Tb³⁺-activated SrF₂ nanophosphors (NPs) were synthesized using the hydrothermal method. Crystallographic characterization using X-ray diffraction confirms the formation of cubic SrF₂ with space group *Fm* $\bar{3}$ *m* for all samples. The FESEM image indicates spherical-shaped particles. Surface functionalization renders that the NPs are dispersible in water. The strong green emission of SrF₂:5% Tb³⁺, 5% Ce³⁺ at 541 nm increases by 50-fold than that of SrF₂:5% Tb³⁺. The resonance energy transfer between Ce³⁺ and Tb³⁺ via multipolar interactions is observed. The energy transfer efficiency and spectral overlap integral are calculated. The absolute quantum yield of SrF₂:5% Tb³⁺, 5% Ce³⁺ is observed to be ~12%. The NPs show excellent biocompatibility towards the HeLa cell line with 70% cell viability. Intercellular uptake of the SrF₂:5% Tb³⁺, 5% Ce³⁺ nanophosphor is fair, and its potential for anti-counterfeiting and forensic fingerprint applications is observed.

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1. Introduction

Recently, rare earth-doped luminescent inorganic materials have become promising in various applications, such as solid-state lighting, displays, photovoltaic devices, sensors, dental applications, biological labeling, security ink, *etc.*^{1–7} The presence of well-shielded intra 4f–4f transitions in rare earth ions are responsible for their unique luminescence properties, such as sharp band emissions, long luminescence lifetime, and excellent stability, making them popular activators.^{8–11} However, they encounter weak luminescence efficacy due to Laporte's forbidden transitions, limiting their applications. Increasing the luminescence efficacy by adopting methods like sensitization, charge compensation, core–shell formation, *etc.* has been reported by many researchers. Luo *et al.* reported enhanced luminescence due to efficient energy transfer from Ce³⁺ to Tb³⁺ in Ce³⁺ and Tb³⁺ co-doped glasses and glass ceramics containing SrF₂ nanocrystals.¹² Likewise, charge compensation and efficient energy transfer from Ce³⁺ to Tb³⁺ or Mn²⁺ in Ca₉ZnLi(PO₄)₇ have also been reported.^{13,14} Similarly, the enhanced luminescence in the white region by the core–shell formation of the lanthanide-doped SrF₂ core and CaF₂ as the shell has

been reported.¹⁵ Amongst them, sensitization by choosing an appropriate sensitizer is an easier way to improve luminescence. For sensitization, Ce³⁺ ions are commonly used as a sensitizer for other rare-earth ions because they have emissions in the range of 300–360 nm, which overlaps with the excitation spectrum of the other rare-earth ions.^{16,17} Tb³⁺ ions, which have an excitation wavelength in the range of 280–450 nm, correspond to the emissions of Ce³⁺ ions.¹⁸ Thus, good energy transfer can occur easily from Ce³⁺ to Tb³⁺ ions, resulting in the enhancement of emission intensity, *i.e.*, Ce³⁺ ions can act as a sensitizer.

Alkaline earth fluorides of cubic type, especially CaF₂, SrF₂, and BaF₂, are excellent host materials for rare earth metal ions. This is due to their outstanding luminescence properties, such as low phonon energies, large band gaps, high stabilities, high ionicities, and ionic conductivities.^{15–22} Many researchers have extensively studied fluoride phosphors because of their ease of synthesis and good luminescence. Zhang's group reported the mesoporous lanthanide doped SrF₂ for luminescence properties and field emission displays. They also reported the synthesis of monodisperse CaF₂:Ce³⁺/Tb³⁺ hollow spheres as smart drug carriers.²³ Ansari *et al.* reported the synthesis of a highly stable water dispersion of CaF₂:Ce/Tb nanocrystals for optical band gap and photoluminescence properties.²⁴ Besides, many research groups have reported the structural, spectroscopic, and cytotoxicity studies of upconverting SrF₂ nanoparticles.^{25–27} Yan *et al.* also reported the single phase SrF₂:Tb³⁺, Eu³⁺ phosphors using the chemical co-precipitation method. They

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studied the high energy efficiency and multi-color emissions, which have potential applications in white light-emitting diodes.²⁸ Another author also reported the luminescent enhancement of Ce³⁺ and Tb³⁺ doped CaF₂ and they analyzed the effect of Li⁺ ion co-doped in the nanoparticles and hyperthermia application of Ce³⁺ doped CaF₂/Fe₃O₄ nanocomposites.²⁰ Several applications, such as security inks and fingerprint detection of the upconverted nanophosphors, have been reported by many researchers.^{29,30} Jin reported the Eu³⁺ doped BaF₂ and SrF₂ nanocrystals for luminescence properties and telecommunication.³¹ An eco-friendly synthesis of SrF₂ nanoparticles and studies on the *in vitro* biocompatibility and antibacterial properties have been reported.³² Eu-doped BaF₂ nanoparticles were used for bioimaging applications.³³ However, reports on multifunctional applications such as biocompatibility, security inks, and fingerprint detection of Ce³⁺ and Tb³⁺ co-doped SrF₂ are still rare.

In this present work, we have chosen SrF₂ as a host matrix, Tb³⁺ as the activator, and Ce³⁺ as the sensitizer for preparing single-phase multifunctional biocompatible luminescent NPs. SrF₂:Tb³⁺, Ce³⁺ nanophosphors have been synthesized using trisodium citrate as a capping agent by a hydrothermal method. The crystal structure, morphology, luminescence properties, quantum yield and energy transfer mechanism were studied. Because of the potential biological applications of synthesized NPs, their cytotoxicity was assessed. The biocompatibility of the as-synthesized nanophosphors was performed on the HeLa cell line. Moreover, intracellular uptakes of our NPs were also analyzed using fluorescence microscopy. Furthermore, luminescence anti-counterfeiting and forensic fingerprint detection were also investigated.

2. Experimental sections

2.1. Reagents and materials

Strontium nitrate (Sr(NO)₃, Sisco-chem, 98.50%), purified ammonium fluoride (NH₄F, Merck), trisodium citrate dihydrate (C₆H₅Na₃O₇·2H₂O, Himedia, 99.00%), terbium(III) nitrate pentahydrate (Tb(NO)₃·5H₂O, Sigma-Aldrich, 99.90%), cerium(III) carbonate hydrate (Ce₂(CO₃)₃·xH₂O, Sigma-Aldrich, 99.90%), ethylene glycol and deionized water were used in the synthesis of the materials. The reagents were analytically pure and used without further purification.

2.2. Synthesis of Sr_{0.90}F₂:5% Tb³⁺, 5% Ce³⁺ (SrF₂:5% Tb³⁺, 5% Ce³⁺) samples

In a typical synthesis of SrF₂:5% Tb³⁺, 5% Ce³⁺ samples, first, a stoichiometric proportion of Ce₂(CO₃)₃·xH₂O (0.048 g) was dissolved in concentrated HNO₃ to obtain its nitrate, and the excess acid was removed by the addition of water, followed by evaporation to dryness. Then, it was dissolved together with a stoichiometric proportion of Sr(NO)₃ (0.676 g) and in 20 mL of 1:1 ethylene glycol and water solution. 20 mL of 1:1 ethylene glycol and aqueous solution of 0.595 g NH₄F were

added and stirred vigorously for 30 min. Thereafter, 20 mL of 1:1 ethylene glycol, an aqueous solution of 0.089 g Tb(NO)₃·5H₂O, 20 mL of 1:1 ethylene glycol and an aqueous solution of 1.176 g C₆H₅Na₃O₇·2H₂O were added. The whole mixture was stirred for another 30 minutes and then transferred to a Teflon-lined autoclave. The vessel was kept in a preheated oven at 140 °C for 2 hours, after which it was removed and cooled to room temperature. The product was collected by centrifugation and washed with deionized water and acetone. Finally, the product was dried at 40 °C for further analysis.

2.3. Cell viability studies: MTT assay

The National Centre for Cell Science (NCCS) in Pune provided the HeLa cancer cell line. The cells were grown in DMEM (Dulbecco's modified Eagle medium) medium containing 10% FBS and 0.1% penicillin-streptomycin at 37 °C in a humidified atmosphere containing 5% CO₂. The biocompatibility and cytotoxicity of nanocomposites were assessed using the MTT {3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyltetrazolium bromide} reduction assay.³⁴ After 48 h of treatment, 15 μL of MTT solution (5 mg mL⁻¹) was added to each well (96 well plate) and incubated for 3 h. During this time, the developed formazan crystals were dissolved by adding 100 μL of DMSO to each well, and absorbance was measured at 570 nm using a Varioskan™ LUX multimode microplate reader.³⁵ Cell viability was calculated as: [A₅₇₀(treated cells) - background]/[A₅₇₀(untreated cells) - background] × 100. Studies were performed in triplicate for each data point.

2.4. Intracellular uptake studies

HeLa cells (5 × 10⁴) were seeded on coverslips placed in the wells of a 6-well plate and treated with different concentrations of NPs for 24 h. The cells were washed with PBS twice, permeabilized with 0.1% Triton X100 for 5 min, and washed with PBS twice. The cells were fixed with 4% paraformaldehyde for 10 min and washed with PBS twice. The fixed cells were stained with DAPI (4,6-diamidino-2-phenylindole) for 5 min in the dark and washed with PBS twice.³⁶ The intracellular uptake imaging of the NPs in HeLa cell lines was performed using fluorescence microscopy.

2.5. Characterization

Powder XRD was carried out on the samples using a PANalytical X-ray diffractometer (X'Pert Pro) Cu (Kα) radiation (λ = 1.5405 Å), 2θ range of 15–90° to determine the identification and purity of the phase. The morphology and size of the synthesized phosphors were observed by FE-SEM (JEOL, JSM 6390LV). An energy dispersive X-ray spectroscopy (EDS/EDX) attached to a Quanta - 250 SEM was used to analyze the elemental composition. The absorption spectra were recorded using a UV-vis spectrophotometer (UV-2600, Shimadzu). Shimadzu IRAffinity 1S was used to record the Fourier transform infrared (FT-IR) spectra. The photoluminescence spectra and their decay



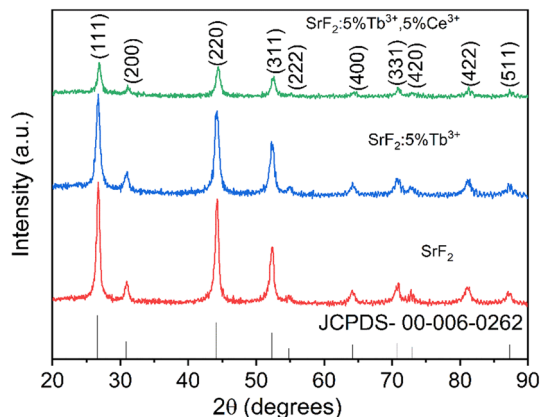


Fig. 1 XRD pattern of SrF₂, SrF₂:5% Tb³⁺, and SrF₂:5% Tb³⁺, 5% Ce³⁺ nanophosphors.

as well as quantum yield (QY) were measured with a Horiba make Fluoromax-4CP spectrofluorometer equipped with an arc xenon lamp 150 W and 5 W microsecond pulse lamp. The QY was measured by integrating the sphere K-sphere 'petite' (Photon Technology International). All the measurements were done in the emission mode. The absolute QY was calculated

using the relation, $\Phi (\%) = \frac{\int I_{\text{emission}} d\lambda}{\int I_{\text{sample holder}} d\lambda - \int I_{\text{sample}} d\lambda}$ where

I_{emission} = luminescence emission intensity of the sample, $I_{\text{sample holder}}$ = the intensity of excitation light only the quartz slide and I_{sample} = the intensity of the light used for exciting the sample placed on the quartz slide. The difference in the denominator gives the photons absorbed by the sample. All the PL measurements were carried out on the glass (for PL and decay lifetime) and quartz slides (for QY) at room temperature. The luminescence decay lifetime for Ce³⁺ emission was measured by the TCSPC technique with Horiba make DeltaFlex having pulse LED laser 295 ± 10 nm as source (pulse width ≤ 1.2 ns).

3. Results and discussions

3.1. XRD studies

Fig. 1 shows the X-ray diffraction patterns of SrF₂, SrF₂:5% Tb³⁺, SrF₂:5% Tb³⁺, 5% Ce³⁺ nanophosphors. The diffraction patterns can be indexed to the standard diffraction data 00-006-0262 for the cubic phase of SrF₂ possessing the *Fm* $\bar{3}$ *m* space group. No additional phases, such as Tb₂O₃, Ce₂O₃, Ce₃O₄, etc., are observed upon adding Tb³⁺ and Ce³⁺ ions into the SrF₂ lattice. The calculated lattice parameters, crystallite sizes, and unit cell volumes are shown in Table 1. The crystallite sizes were

calculated using the Scherrer formula: $d = k\lambda/\beta \cos \theta$. The strongest peak corresponding to the (111) plane was used to calculate the average crystallite size of the samples. Again, using the Williamson–Hall model, the crystallite sizes were also calculated, which were almost similar to those calculated using the Scherrer formula. From Table 1, it is observed that the unit cell volume is increased on Tb³⁺ substitution, whereas the ionic radius of the Sr²⁺ ion (1.32 Å) is larger than that of Tb³⁺ (0.92 Å) at coordination number 6.³⁷ Our result is contradictory to the Vegard's law; the unit cell volume must be slightly decreased as compared to that of pure SrF₂. This is due to the occupancy of the excess fluoride ions in the interstitial sites, which compensate for the excess positive charge due to the substitution of trivalent lanthanide ions at Sr²⁺ sites. The balanced chemical equation can be represented as $2\text{Sr}^{2+} \rightarrow \text{Ln}^{3+} + \text{F}^-$. It may also be due to the formation of tetragonal (*C*_{4v}) or trigonal (*C*_{3v}) and electronic repulsions between F⁻ ions, which leads to the expansion of unit cell volume.^{38,39} However, a small increase in the unit cell volume is observed for Ce³⁺ and Tb³⁺ co-doped SrF₂ NPs, which is due to the ionic radius of Ce³⁺ (1.01 Å) ion being greater than that of Tb³⁺ ion (0.92 Å) at coordination number 6.^{37,40}

3.2. FESEM and EDS studies

The morphologies of the SrF₂:5% Tb³⁺, 5% Ce³⁺ nanophosphors were studied by FESEM imaging, as shown in Fig. 2(a). The FESEM image shows the formation of spherical-shaped nanoparticles with a particle size range of 50–60 nm. Fig. 2(b) shows the typical histogram of the particle diameter (size) for the sample SrF₂:5% Tb³⁺, 5% Ce³⁺. The energy dispersive spectra of SrF₂, SrF₂:5% Tb³⁺, SrF₂:5% Ce³⁺, and SrF₂:5% Tb³⁺, 5% Ce³⁺ nanophosphors, respectively, are shown in Fig. 2(c–f). The Sr, F, Ce, and Tb elements are detected from the respective nanophosphor samples, indicating the successful preparation of Tb³⁺ and Ce³⁺ co-doped SrF₂ NP.

3.3. FT-IR studies

Fig. 3 shows the FT-IR spectrum of the as-prepared SrF₂:5% Tb³⁺, 5% Ce³⁺ nanophosphors. The strong single broad peak at around 3600–3300 cm⁻¹ corresponds to the O–H bond stretching vibration of the ethylene glycol/H₂O used as a solvent. The peaks at 1069–1252 cm⁻¹ correspond to the CH₂ bending from ethylene glycol.⁴¹ Other bands at 1401 and 1575 cm⁻¹ arise from the symmetric and asymmetric vibrations of COO⁻ from the capping agent added during the synthesis, which gets adsorbed on the surface of the particles.⁴² The band at 460

Table 1 Lattice parameters and crystallite sizes of SrF₂, SrF₂:5% Tb³⁺, and SrF₂:5% Tb³⁺, 5% Ce³⁺ nanophosphors

Sample	Lattice parameter <i>a</i> (Å)	Unit cell volume (Å ³)	Crystallite size (nm)	
			Debye	Williamson
Reference JCPDS 00-006-0262 SrF ₂	5.80	195.11		
SrF ₂	5.76	191.76	10	12
SrF ₂ :5% Tb ³⁺	5.77	192.19	8	9
SrF ₂ :5% Tb ³⁺ , 5% Ce ³⁺	5.78	193.58	7	8



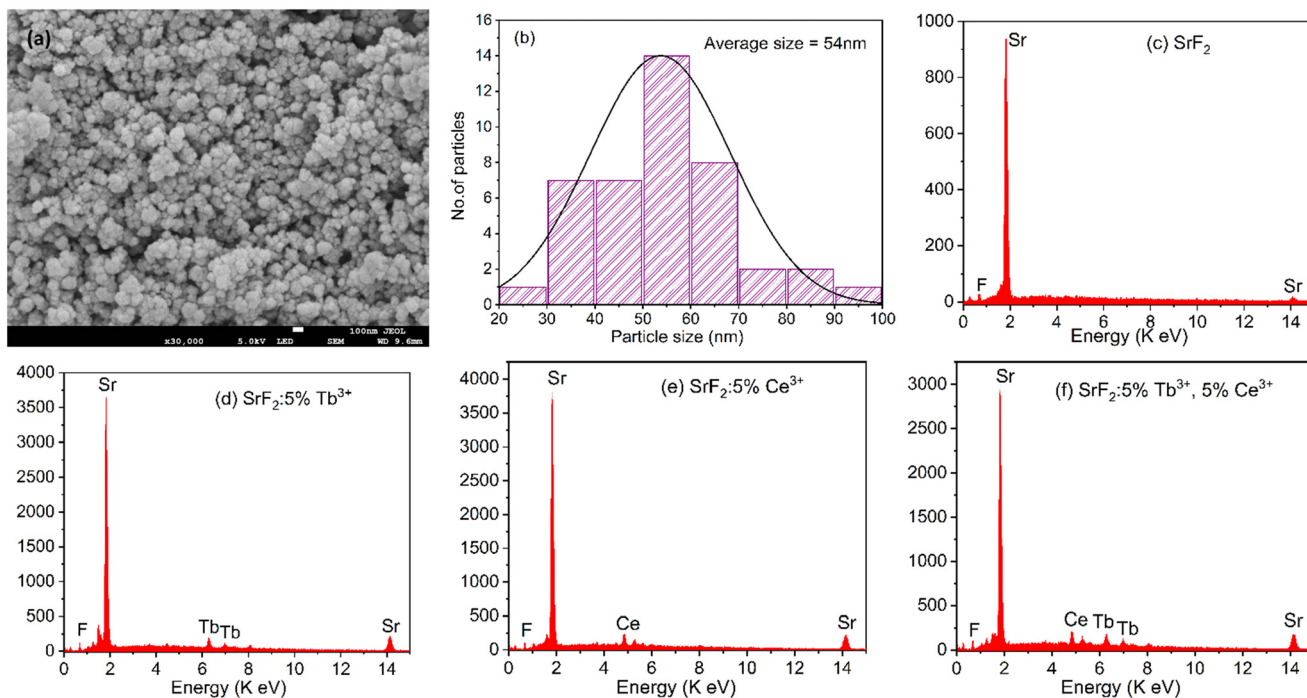


Fig. 2 (a) FESEM image, (b) histogram of the particle diameters, and (c)–(f) energy dispersive spectrum (EDS) of SrF_2 , $\text{SrF}_2:5\% \text{Tb}^{3+}$, $\text{SrF}_2:5\% \text{Ce}^{3+}$ and $\text{SrF}_2:5\% \text{Tb}^{3+}, 5\% \text{Ce}^{3+}$ nanophosphors.

cm^{-1} is assigned to the Sr–F stretching vibration. The presence of ethylene glycol and trisodium citrate dihydrate, along with the NPs, will help in the incorporation/dispersion of NPs in polar media and thin films.

3.4. Optical studies

The absorption spectra of the as-synthesized SrF_2 , $\text{SrF}_2:5\% \text{Tb}^{3+}$, and $\text{SrF}_2:5\% \text{Tb}^{3+}, 5\% \text{Ce}^{3+}$ nanophosphors are shown in Fig. 4. The NPs show a strong absorption in the UV spectral region of 200–400 nm. It is observed that there is a peak at around 235 to 256 nm, with the maximum at 245 nm in Tb^{3+} doped SrF_2 NPs. On the other hand, for Ce^{3+} co-

doped Tb^{3+} doped SrF_2 NPs, in addition to the above peak, there is another peak at 281 to 306 nm with the maximum at 293 nm. Since the optical bandgap of SrF_2 is ~ 11 eV,⁴³ the absorption band lies in the vacuum UV region, which is beyond our spectrophotometer detection capability. Therefore, the corresponding absorption bands observed in the region above may be related to the defect states localized in the forbidden region of SrF_2 . Researchers have already reported similar studies on unactivated CaF_2 , SrF_2 , BaF_2 and lanthanide-activated CaF_2 .^{44,45} As Mukherjee *et al.* have reported in the lanthanide-activated CaF_2 ,⁴⁴ these defect states may arise from the creation of vacancies to maintain charge neutrality during the substitution of Sr^{2+} sites by Ce^{3+}

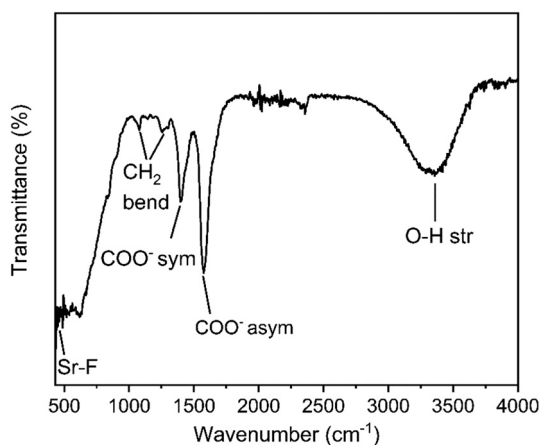


Fig. 3 FT-IR spectrum of $\text{SrF}_2:5\% \text{Tb}^{3+}, 5\% \text{Ce}^{3+}$ nanophosphors.

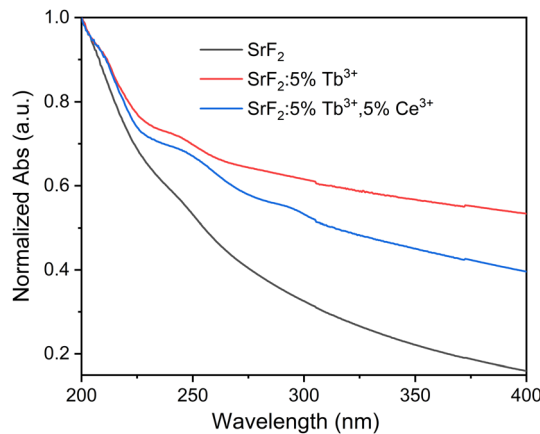


Fig. 4 UV-vis spectra of SrF_2 , $\text{SrF}_2:5\% \text{Tb}^{3+}$, and $\text{SrF}_2:5\% \text{Tb}^{3+}, 5\% \text{Ce}^{3+}$ nanophosphors.



and/or Tb^{3+} . Also, F-interstitial sites may act as defect sites during lanthanide substitution for charge compensation (as the F^- source was taken 2 times its molar requirement).

3.5. Photoluminescence (PL) studies

PL excitation spectra of $\text{SrF}_2:5\% \text{Ce}^{3+}$, $\text{SrF}_2:5\% \text{Tb}^{3+}$ and $\text{SrF}_2:5\% \text{Tb}^{3+}, 5\% \text{Ce}^{3+}$ nanophosphors monitored at the emission wavelengths at 330 nm (for $\text{SrF}_2:5\% \text{Ce}^{3+}$) and 541 nm for the remaining 2 (two) are displayed in Fig. 5(a). The excitation spectrum of $\text{SrF}_2:5\% \text{Ce}^{3+}$ consists of two broad excitation bands in the range of 230 to 320 nm, with the maximum peaks at 260 and 297 nm, corresponding to the spin-allowed 4f–5d transitions of Ce^{3+} ions. These are originated from the transitions of $^2\text{F}_{5/2}$ and $^2\text{F}_{7/2}$ ground states to the $^2\text{D}_{3/2}$ and $^2\text{D}_{5/2}$ excited states of 5d orbitals.⁴⁶ Though, the excitation spectrum of $\text{SrF}_2:5\% \text{Tb}^{3+}$ shows a broad peak at 250–260 nm, which corresponds to the 4f–5d and Tb–O charge transfer.⁸ In addition, the excitation peaks observed in the longer wavelength region at 349 ($^7\text{F}_6 \rightarrow ^5\text{D}_1$), 355 ($^7\text{F}_6 \rightarrow ^5\text{D}_1$), 363 ($^7\text{F}_6 \rightarrow ^5\text{D}_1$) and 370 ($^7\text{F}_6 \rightarrow ^5\text{D}_1$) nm are associated with the 4f–4f transitions of Tb^{3+} ions from the $^7\text{F}_6$ ground state to the different higher excited states. Meanwhile, the $\text{SrF}_2:5\% \text{Tb}^{3+}, 5\% \text{Ce}^{3+}$ sample shows two main absorption peaks at 260 and 297 nm. These peaks are related to the spin-allowed 4f–5d transitions of Ce^{3+} (as discussed above). Here, the 4f–5d transition and/or Tb–O charge transfer band of Tb^{3+} is not seen, as it might have merged with the 260 nm excitation peak due to Ce^{3+} . The excitation peaks are also observed in the longer wavelength region due to absorption within the Tb^{3+} ions (as discussed above). The strong excitation peak at 260 and 297 nm related to Ce^{3+} indicates the strong energy transfer from Ce^{3+} to the excited states of Tb^{3+} . Fig. 5(b) shows the normalized excitation spectra of $\text{SrF}_2:5\% \text{Ce}^{3+}$, $\text{SrF}_2:5\% \text{Tb}^{3+}$ and $\text{SrF}_2:5\% \text{Tb}^{3+}, 5\% \text{Ce}^{3+}$ at different emission peaks related to their characteristic emissions, *i.e.*, 330 nm for Ce^{3+} and 488 ($^5\text{D}_4 \rightarrow ^7\text{F}_6$), 541 ($^5\text{D}_4 \rightarrow ^7\text{F}_5$), 583 ($^5\text{D}_4 \rightarrow ^7\text{F}_4$) and 620 ($^5\text{D}_4 \rightarrow ^7\text{F}_3$) nm

of Tb^{3+} to check any additional peaks, which can be correlated to the Ce^{3+} (sensitizer/donor) emission. Here, it is observed that excitation bands related to the Ce^{3+} emission are observed only in $\text{SrF}_2:5\% \text{Ce}^{3+}$ and $\text{SrF}_2:5\% \text{Tb}^{3+}, 5\% \text{Ce}^{3+}$. Such a band is not observed in $\text{SrF}_2:5\% \text{Tb}^{3+}$.

The PL emission spectra of $\text{SrF}_2:5\% \text{Ce}^{3+}$, $\text{SrF}_2:5\% \text{Tb}^{3+}$ and $\text{SrF}_2:5\% \text{Tb}^{3+}, 5\% \text{Ce}^{3+}$ nanophosphors under different excitation wavelengths are shown in Fig. 6(a). For $\text{SrF}_2:5\% \text{Ce}^{3+}$, the excitation wavelengths are 260 and 297 nm. Both spectra show the characteristic emission of Ce^{3+} in the range of 300–400 nm with a maximum at 330 nm. This is due to the transition from the excited d-level to the f-level ground state of Ce^{3+} . On the other hand, excitation wavelengths for $\text{SrF}_2:5\% \text{Tb}^{3+}$ are related to the Tb^{3+} absorption at 255 and 370 nm. The characteristic emission peaks of Tb^{3+} are seen at 488 ($^5\text{D}_4 \rightarrow ^7\text{F}_6$), 541 ($^5\text{D}_4 \rightarrow ^7\text{F}_5$), 583 ($^5\text{D}_4 \rightarrow ^7\text{F}_4$) and 620 ($^5\text{D}_4 \rightarrow ^7\text{F}_3$) nm. Meanwhile, the emission spectra for $\text{SrF}_2:5\% \text{Tb}^{3+}, 5\% \text{Ce}^{3+}$ were recorded under the excitation of 260, 297, and 370 nm. Here, all the emissions related to Ce^{3+} and Tb^{3+} are observed. However, the Ce^{3+} emission intensity is drastically reduced compared to $\text{SrF}_2:5\% \text{Ce}^{3+}$, while the Tb^{3+} -related emission peaks are enhanced when compared to $\text{SrF}_2:5\% \text{Tb}^{3+}$. Thus, it suggests the efficient energy transfer from the Ce^{3+} excited states to the excited states of Tb^{3+} ions (discussed later).⁴⁷ The emission peak corresponding to $^5\text{D}_4 \rightarrow ^7\text{F}_5$ at 541 nm is dominant over others; therefore, the overall emission color is green. The emission intensity of $\text{SrF}_2:5\% \text{Tb}^{3+}, 5\% \text{Ce}^{3+}$ is found to be enhanced ~ 50 times than that of $\text{SrF}_2:5\% \text{Tb}^{3+}$ under similar radiation exposure.

According to Dexter's theory,⁴⁸ the spectral overlap between the excitation spectrum of the activator and the emission spectrum of the sensitizer is required to support the energy transfer from sensitizer to the activator. Therefore, we demonstrated the normalized spectral overlap between the $\text{SrF}_2:5\% \text{Tb}^{3+}$ excitation and $\text{SrF}_2:5\% \text{Ce}^{3+}$ emission, as shown in Fig. 6(b). A broad spectral overlap between these two spectra in the wavelength ranges from 300 to 450 nm, indicating the occurrence of efficient energy transfer from

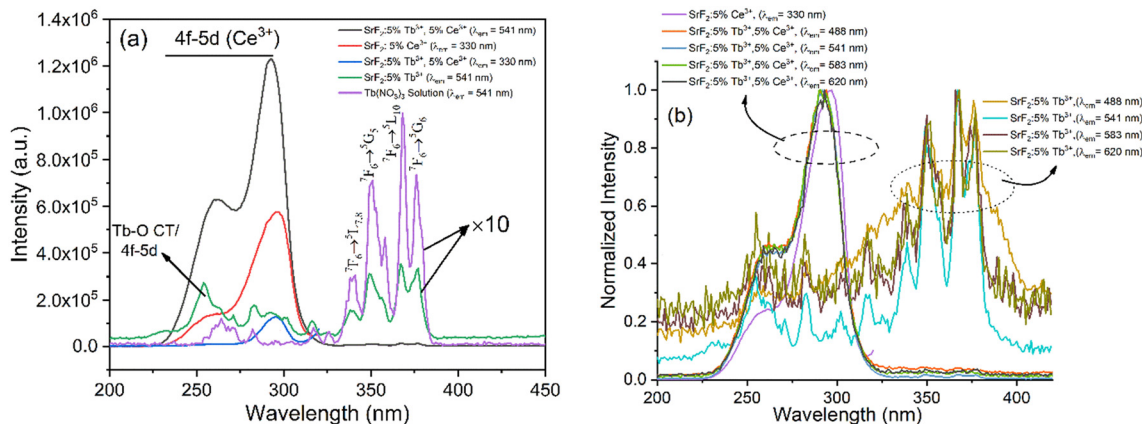


Fig. 5 (a) Excitation spectra of $\text{SrF}_2:5\% \text{Tb}^{3+}$, $\text{SrF}_2:5\% \text{Ce}^{3+}$ and $\text{SrF}_2:5\% \text{Tb}^{3+}, 5\% \text{Ce}^{3+}$ (b) normalized excitation spectra of $\text{SrF}_2:5\% \text{Tb}^{3+}$, $\text{SrF}_2:5\% \text{Ce}^{3+}$ and $\text{SrF}_2:5\% \text{Tb}^{3+}, 5\% \text{Ce}^{3+}$ samples at all the emission peaks.



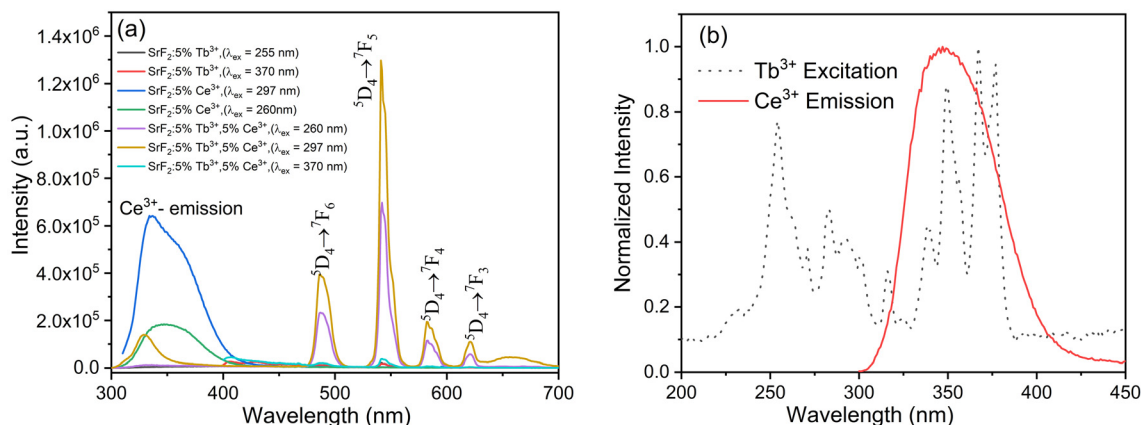


Fig. 6 (a) Emission spectra of SrF₂:5% Tb³⁺, SrF₂:5% Ce³⁺ and SrF₂:5% Tb³⁺, 5% Ce³⁺ nanophosphors and (b) normalized spectral overlap of SrF₂:5% Ce³⁺ emission and SrF₂:5% Tb³⁺ excitation.

Ce³⁺ to Tb³⁺ ions in SrF₂:5% Tb³⁺, 5% Ce³⁺.^{49,50} The probable energy transfer mechanism is shown in Fig. 7. The sensitization of Tb³⁺ by Ce³⁺ in SrF₂ may also occur *via* a charge trap-mediated process. Such an energy transfer process was illustrated by Mukherjee *et al.* in Tb³⁺/Eu³⁺ co-doped CaF₂.⁴⁴ Here, the sensitization of Tb³⁺ by Ce³⁺ in SrF₂ may also occur *via* a charge trap-mediated process where the photogenerated electron from the initially excited Ce³⁺ energy level recombines with a photogenerated hole at the Tb³⁺ center and thus populates the Tb³⁺ luminescent energy level ⁵D₄. Later, the radiative transition occurs from the excited state ⁵D₄ to the ground states with enhanced emission.

The PL decay lifetime curves of the SrF₂:5% Ce³⁺ and SrF₂:5% Tb³⁺, 5% Ce³⁺ samples at 295 ± 10 nm excitation when the emission is monitored at 330 nm along with the instrument response function (IRF) are shown in Fig. 8(a). The decay lifetime values of SrF₂:5% Ce³⁺, SrF₂:5% Tb³⁺, 5% Ce³⁺ samples were calculated using eqn (1)

$$I(t) = I_0 \exp(-t/\tau) \quad (1)$$

The decay lifetimes are found to be ~15.35 and 7.82 ns, respectively, whereas the value of IRF is ~1.7 ns. The typical curve fitting using eqn (1) is shown in Fig. 8(b). The PL decay

lifetime of Ce³⁺ is decreased in the presence of Tb³⁺. This is due to the non-radiative excited electron transfer from the excited states of Ce³⁺ to the excited states of Tb³⁺ at the expense of radiative transition to the ground state within Ce³⁺. Thus, this establishes the occurrence of energy transfer from Ce³⁺ to Tb³⁺. Further, this corroborates the existence of energy transfer discussed in steady-state PL studies. The energy transfer efficiency (φ) was calculated from the lifetime values using⁵¹

$$\varphi = 1 - \frac{\tau_s}{\tau_{s0}} \quad (2)$$

where τ_s and τ_{s0} are the lifetimes of Ce³⁺ in the presence and absence of Tb³⁺, respectively. The φ is found to be 49%. Fig. 9(a and b) shows the PL decay curves of the ⁵D₄ level of Tb³⁺ for the SrF₂:5% Tb³⁺ and SrF₂:5% Tb³⁺, 5% Ce³⁺ at 370 nm excitation when the emission is monitored at 541 nm. Fig. 9(c) shows the decay curve of the SrF₂:5% Tb³⁺, 5% Ce³⁺ sample at 297 nm excitation when the emission is monitored at 541 nm. The following decay equation was used to calculate the PL decay lifetime:⁵¹

$$I = I_0 \exp\left(-\frac{t}{\tau}\right) - (2bt^{\frac{1}{2}}) \quad (3)$$

Here, I and I_0 represent the emission intensities at a given time, ' t ' and $t = 0$, respectively, and ' b ' is the quencher concentration dependent on diffusion co-efficient, while the power of ' t ' is taken $\frac{1}{2}$ as the energy transfer is assumed to be resonance type. ' τ ' is the PL decay lifetime. The PL decay lifetime values of the SrF₂:5% Tb³⁺ and SrF₂:5% Tb³⁺, 5% Ce³⁺ samples at 370 nm excitation when the emission is monitored at 541 nm were found to be 4.10 and 4.56 ms, respectively. The lifetime values of the SrF₂:5% Tb³⁺, 5% Ce³⁺ samples at 297 nm excitation when the emission is monitored at 541 nm was found to be ~6 ms.

Generally, the energy transfer between Ce³⁺ and Tb³⁺ is possible *via* two mechanisms: exchange interaction and multipolar interaction. The distance between the donor and the acceptor plays an important role in determining the probable type of energy transfer. This can be checked by

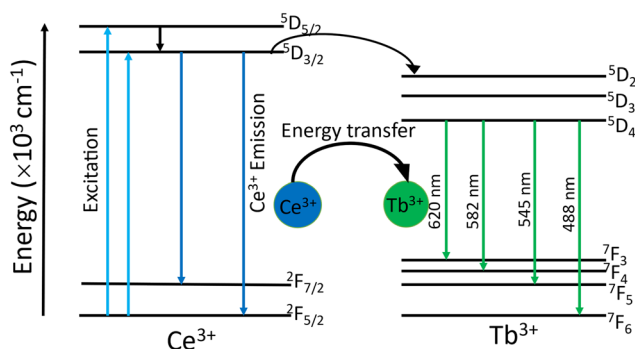


Fig. 7 Schematic energy transfer pathways from Ce³⁺ to Tb³⁺.



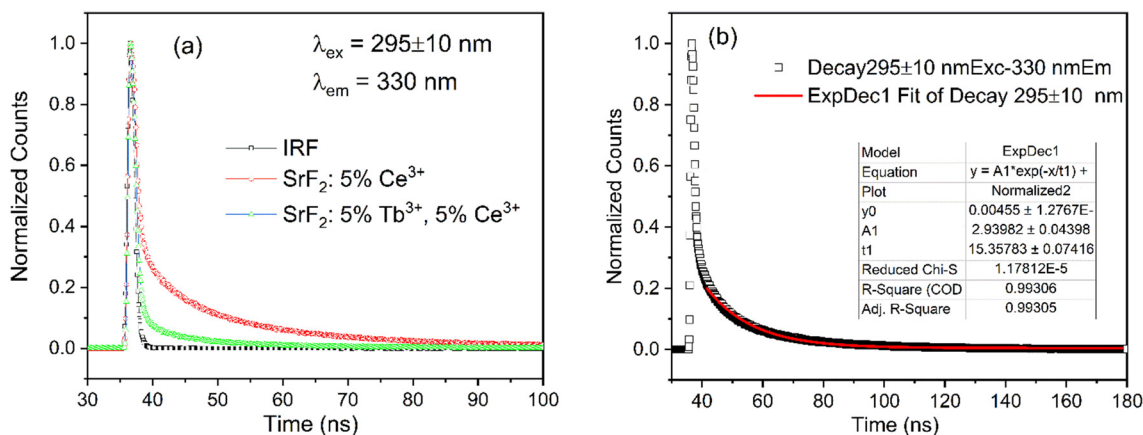


Fig. 8 (a) Decay profile of IRF, SrF₂:5% Ce³⁺ and SrF₂:5% Tb³⁺, 5% Ce³⁺ samples excited at 295 ± 10 nm and emission is monitored at 330 nm, (b) decay profile of SrF₂:5% Ce³⁺ nanophosphors excited at 295 ± 10 nm and emission is monitored at 330 nm.

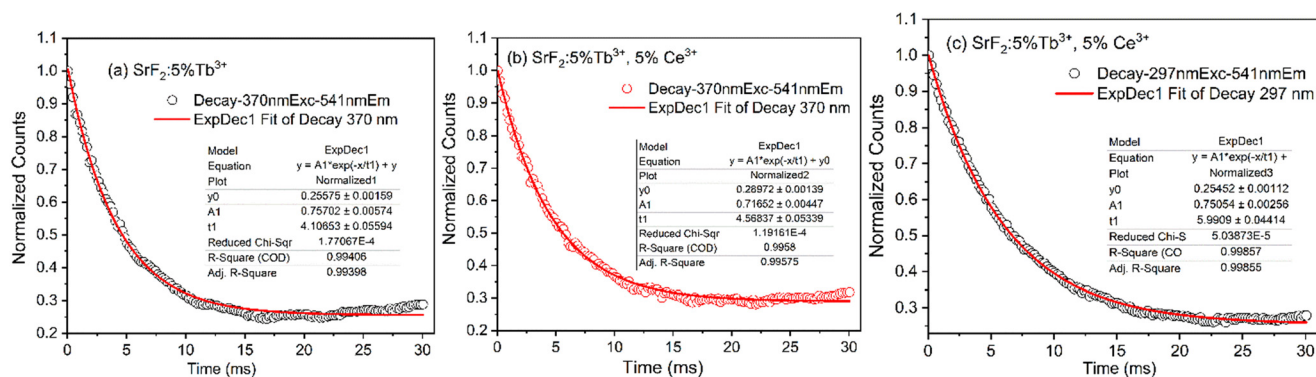


Fig. 9 (a and b) Decay profile of SrF₂:5% Tb³⁺ and SrF₂:5% Tb³⁺, 5% Ce³⁺ nanophosphors excited at 370 nm and emission is monitored at 541 nm and (c) decay profile of SrF₂:5% Tb³⁺, 5% Ce³⁺ samples excited at 297 nm and emission is monitored at 541 nm.

calculating the critical distance (R_c) between Tb³⁺ and Ce³⁺ ions, using the following equation,^{52,53}

$$R_c = 2 \left(\frac{3V}{4\pi X_c N} \right)^{1/3} \quad (4)$$

where V represents the unit cell volume, X_c is the concentration and N is the number of the cations at the center of the unit cell in the host. In the SrF₂ host lattice, the unit cell volume is 193.58 Å³, the total concentration is 10% and the value of N is 4. The calculated value of R_c using eqn (4) is found to be 9.7 Å, which is larger than 5 Å. This indicates the energy transfer mechanism from Ce³⁺ to the excited state of Tb³⁺ in the SrF₂ is dominated by multipolar interactions; thereby, the exchange interaction type of energy transfer can be ignored.⁵³

To further elucidate the resonance energy transfer, the overlap spectral integral ($J(\lambda)$), which is the expression of the degree of spectral overlap between the donor emission and the acceptor absorption, can be calculated as⁵¹

$$J(\lambda) = \int_0^\infty F_D(\lambda) \varepsilon_A(\lambda) \lambda^4 d\lambda = \frac{\int_0^\infty F_D(\lambda) \varepsilon_A(\lambda) \lambda^4 d\lambda}{\int_0^\infty F_D(\lambda) d\lambda} \quad (5)$$

$F_D(\lambda)$ is the luminescence intensity of the donor and is dimensionless. $\varepsilon_A(\lambda)$ is the molar extinction coefficient of the acceptor in M⁻¹ cm⁻¹, and λ is expressed in nanometre. According to Förster's resonance energy transfer theory, the energy transfer efficiency (φ) is dependent on the distance between the donor and acceptor (R_c),⁵¹

$$\varphi = \frac{R_0^6}{R_0^6 + R_c^6} \quad (6)$$

where R_0 is the Förster critical distance, which is defined as the distance for φ to be 50%. Using eqn (6) and with the obtained $\varphi = 49\%$ and $R_c = 9.7$ Å, the R_0 is calculated to be 9.8 Å. Again, R_0 can be further defined as follows:⁵¹

$$R_0^6 = 8.79 \times 10^{-5} (\kappa^2 n^{-4} \eta_D J(\lambda)) \quad (7)$$

where ' n ' is the refractive index of the medium (here, SrF₂), κ^2 is the relative dipole orientation in the space of the transition dipoles of the donor and acceptor and is usually assumed to be $\frac{2}{3}$. η_D is the quantum yield of the donor in the absence of the acceptor. The spectral integral ($J(\lambda)$) is expressed in M⁻¹ cm⁻¹ nm⁴. Using eqn (7) and taking ' n ' =



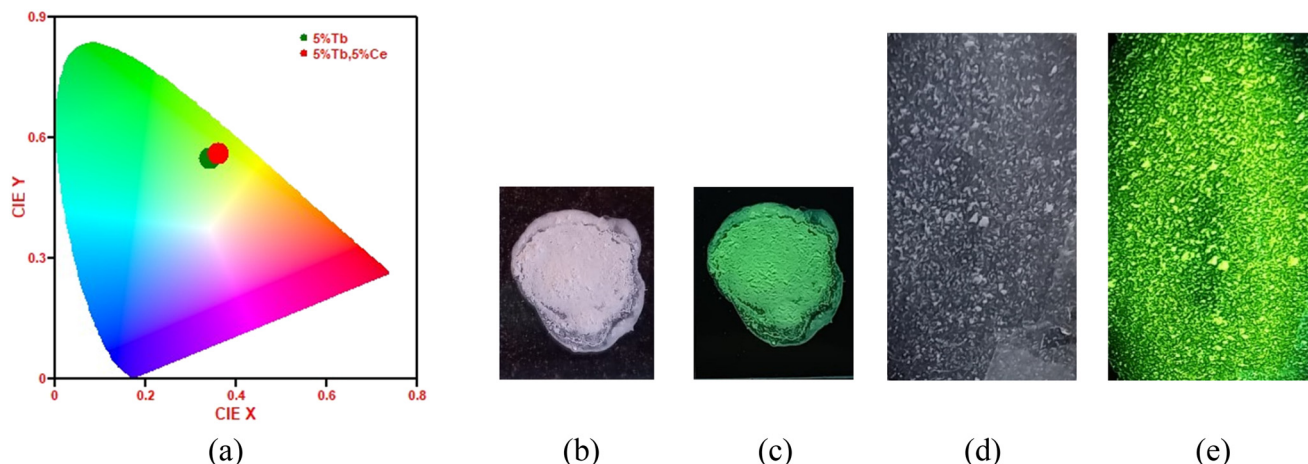


Fig. 10 (a) CIE chromaticity diagram of $\text{SrF}_2:5\% \text{Tb}^{3+}$ and $\text{SrF}_2:5\% \text{Tb}^{3+}, 5\% \text{Ce}^{3+}$ nanophosphors excited at 255 nm. (b) and (d) Before exposure and (c) and (e) after exposure of powder and a thin film of the $\text{SrF}_2:5\% \text{Tb}^{3+}, 5\% \text{Ce}^{3+}$ nanophosphors, respectively.

1.48 and $\eta_D = 22\%$ (given in the next paragraph), $J(\lambda)$ is calculated to $1.05 \times 10^{10} \text{ M}^{-1} \text{ cm}^{-1} \text{ nm}^4$. It is also stated that if $0.5R_0 < R_c < 2R_0$, efficient energy transfer occurs.^{53b}

3.6. CIE chromaticity coordinates and quantum yield efficiency

The calculated CIE coordinates diagram of $\text{SrF}_2:5\% \text{Tb}^{3+}$ and $\text{SrF}_2:5\% \text{Tb}^{3+}, 5\% \text{Ce}^{3+}$ nanophosphors excited at 255 nm are shown in Fig. 10(a). The corresponding chromaticity coordinates for $\text{SrF}_2:5\% \text{Tb}^{3+}$ and $\text{SrF}_2:5\% \text{Tb}^{3+}, 5\% \text{Ce}^{3+}$ nanophosphors, respectively, are $(x = 0.34, y = 0.55)$ and $(x = 0.36, y = 0.56)$. It can be seen that the emission of Tb^{3+} ions and Ce^{3+} ions co-doped SrF_2 nanophosphors corresponds to the green color. Moreover, as the Ce^{3+} ions co-doped into the Tb^{3+} ions doped SrF_2 nano-phosphor, the intensity of emission change is observed while the luminescence color is hardly changed. Fig. 10(b and c) shows the powder photographic image of the $\text{SrF}_2:5\% \text{Tb}^{3+}, 3\% \text{Ce}^{3+}$ phosphor before and after 254 nm UV irradiation, suggesting the bright green color as suggested from the CIE diagram. We also prepared a thin film of the $\text{SrF}_2:5\% \text{Tb}^{3+}, 3\% \text{Ce}^{3+}$ phosphor by using 5 mg of 10% PVA and borax solution. The physical photographic image of a thin film is shown in Fig. 10(d and e). The colour correlated temperature (CCT) was calculated by using the following equation:⁵⁴

$$\text{CCT} = -437n^3 + 3601n^2 - 6861n + 5517$$

and

$$n = (x - 0.3320)/(0.1858 - y) \quad (8)$$

where x and y are the color coordinates.

The CCT values are found to be 5368 and 5023 for the $\text{SrF}_2:5\% \text{Tb}^{3+}$ and $\text{SrF}_2:5\% \text{Tb}^{3+}, 5\% \text{Ce}^{3+}$ nanophosphors, and the values lie in the cold white region. Therefore, the as-prepared samples have a potential application in WLEDs. The absolute method was used to measure the quantum yield efficiency of the $\text{SrF}_2:5\% \text{Tb}^{3+}, 5\% \text{Ce}^{3+}$ and $\text{SrF}_2:5\% \text{Ce}^{3+}$ phosphor using an integrating sphere. The value is found to be $\sim 12\%$ and 22% , respectively. Fig. 11(a and b) shows the quantum yield values of $\text{SrF}_2:5\% \text{Tb}^{3+}, 5\% \text{Ce}^{3+}$ and $\text{SrF}_2:5\% \text{Ce}^{3+}$ nanophosphors from the instrument, respectively.

3.7. Cell viability studies: MTT assay

The cell viability of the $\text{SrF}_2:5\% \text{Tb}^{3+}, 5\% \text{Ce}^{3+}$ nanophosphor was carried out using HeLa cells by the MTT assay method as shown in Fig. 12. Different concentrations ($6\text{--}200 \mu\text{g mL}^{-1}$) of the nanophosphors were added to the cells and incubated for 24 h. At lower concentrations ($6\text{--}25 \mu\text{g mL}^{-1}$), $>70\%$ of cells were viable, while at higher concentrations

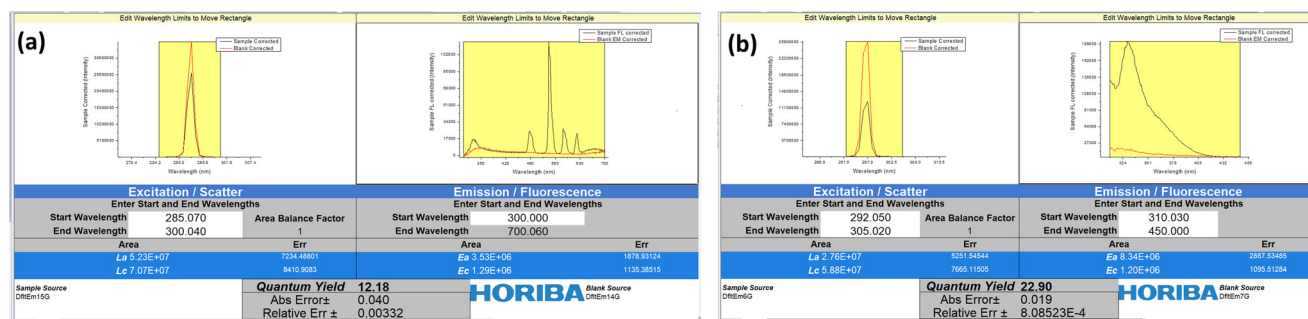


Fig. 11 Calculation of quantum yield for (a) $\text{SrF}_2:5\% \text{Tb}^{3+}, 5\% \text{Ce}^{3+}$ and (b) $\text{SrF}_2:5\% \text{Ce}^{3+}$ nanophosphors using FluorEssence™ software in Horiba Fluoromax-4CP spectrofluorometer.



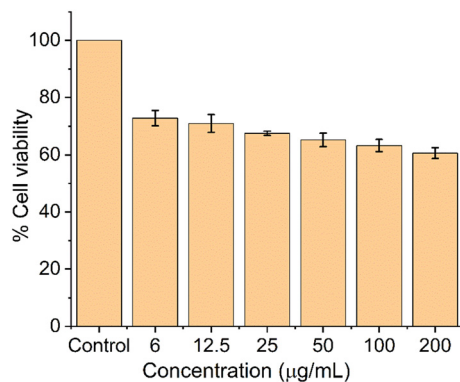


Fig. 12 Cell viability studies using HeLa cells at various SrF₂:5% Tb³⁺, 5% Ce³⁺ nano-phosphor concentrations.

(50–200 µg mL⁻¹), >65% viability was observed. These data suggest the as-prepared nanophosphors displayed good cell viability over a wide concentration range.

3.8. Intracellular uptake studies in HeLa cells by fluorescence microscopy

Since SrF₂:5% Tb³⁺, 5% Ce³⁺ nano-phosphor showed good biocompatibility towards HeLa cells, we decided to investigate the cellular uptake studies of the as-prepared nano-phosphor. Fig. 13 shows the intracellular uptake of the samples (100, 200, and 300 µg mL⁻¹ concentrations) in HeLa cells after a 24-hour incubation period. Fluorescence microscopy was used to track the cellular uptake and internalization of the phosphor samples. The nuclei of the cells were counterstained with the DAPI dye (blue color) to help mark the locations of the cells under fluorescence microscopy. The green fluorescence from the sample-treated cell indicated the incorporation of the samples into HeLa cells. We also note that the blue and green colors are co-localized, which clearly shows that most of the phosphor samples internalize into the nuclei of the cells and not the cytosol. The intensity of the green fluorescence increased with increasing concentration of the phosphor samples, indicating a concentration-dependent nuclear accumulation. This study demonstrated that cultured cells easily internalize phosphor samples, predominantly into the nuclei.

3.9. Applications for fingerprint detection and security ink

In addition to a high intracellular image, practical use of the visible fingerprint image of the SrF₂:5% Tb³⁺, 5% Ce³⁺ phosphor was also carried out. Nowadays, fingerprint detection is the most important evidence in any criminal investigation. In this paper, we use the SrF₂:5% Tb³⁺, 5% Ce³⁺ nano-phosphor for fingerprint detection on a glass slide, which is shown in Fig. 14(a and b). The powder sample was sprinkled on the surface of the glass slide and wiped out softly. The image was recorded under the 254 nm UV light. The fingerprint image of the sample before and after the irradiation of 254 nm UV light can be easily recognized by the naked eye, suggesting the as-prepared phosphor can have a potential application in forensic science.

Moreover, the as-prepared phosphor was also demonstrated in the security ink for an anti-counterfeiting application. The rare-earth-doped particles show visible emissions, thus, they have received attention for anti-counterfeiting applications. The invisible ink was prepared by dispersing 10 mg of the as-prepared phosphor in 2 mL of 10% PVA solution. The mixed solution was sonicated in an ultrasonic bath for 30 minutes to obtain a homogeneous dispersion. Then, a few words like MU were written with this ink, as shown in Fig. 14(c and d). Under daylight, the sample containing ink was invisible (Fig. 14c). But the green-colored MU patterns (Fig. 14d) can be observed under the irradiation of 254 nm UV light, indicating the as-prepared phosphor is highly compatible with anti-counterfeiting performance.

4. Conclusions

In conclusion, we have reported the synthesis and characterization, including biocompatibility studies of SrF₂:Tb³⁺, Ce³⁺ nanophosphors. XRD patterns show the formation of the cubic phase of SrF₂ NPs. A small increase in the unit cell volume is observed with Ce³⁺ and Tb³⁺ co-doping due to excess fluoride ions in the interstitial sites of the host matrix. FESEM micrographs show the formation of spherical-shaped NPs. From FTIR, it is concluded that the capping agent, *i.e.*, trisodium citrate, is present in the as-prepared NPs. A defect-generated broad absorption is observed with good dispersibility in the optical studies. The phosphors show a strong green emission at 541 nm upon excitation at 297 nm, which is due to efficient

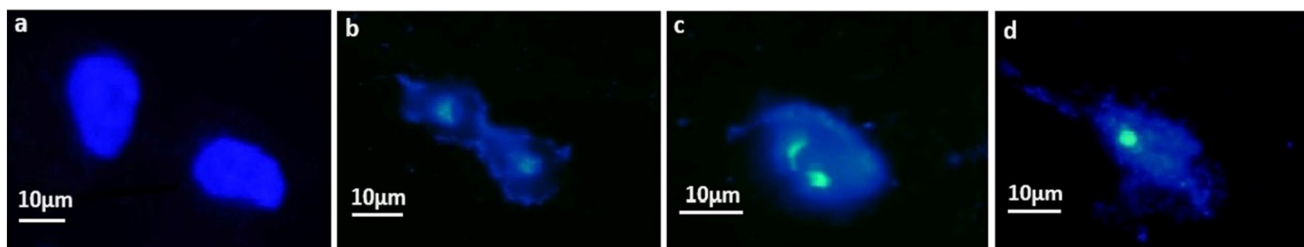


Fig. 13 Fluorescence microscopy imaging of HeLa cells after a 24 h incubation with varying concentrations of phosphor samples. (a) Untreated cells, (b) 100 µg mL⁻¹, (c) 200 µg mL⁻¹, and (d) 300 µg mL⁻¹ of SrF₂:5% Tb³⁺, 5% Ce³⁺ nano-phosphor. The nuclei are stained with DAPI (blue), while the phosphor samples exhibited green color.



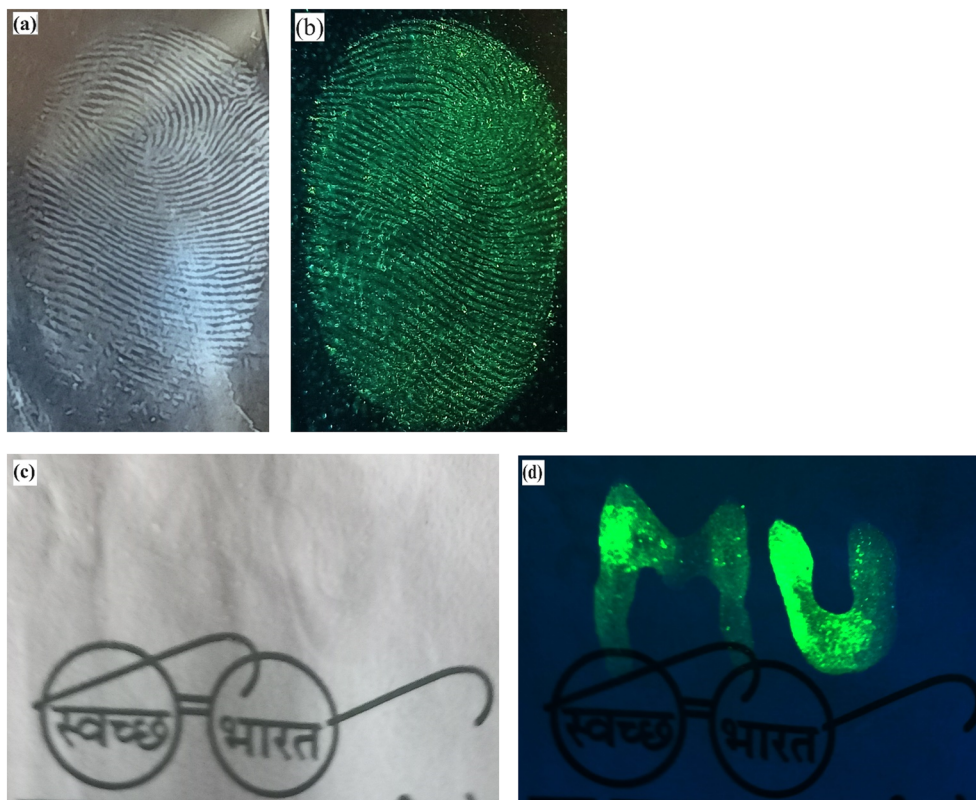


Fig. 14 Demonstration of fingerprint detection on (a and b) glass slide and (c and d) security ink for anti-counterfeiting application using SrF₂:5% Tb³⁺, 5% Ce³⁺ nanophosphors before and after 254 nm UV irradiation.

energy transfer from Ce³⁺ (⁵D_{5/2}) to Tb³⁺ (⁵D₂) ions. With Ce³⁺ co-doping, Tb³⁺ lifetime increases to 6 ms while Ce³⁺ lifetime decreases from 15.35 and 7.82 ns. The energy transfer efficiency and the spectral overlap integral calculated were found to be 49% and $1.05 \times 10^{10} \text{ M}^{-1} \text{ cm}^{-1} \text{ nm}^4$. The synthesized phosphors have excellent biocompatibility towards the HeLa cell line and their cellular uptake was studied. Using the 254 nm wavelength excitation, the applicability of synthesized NPs towards security inks as anti-counterfeiting patterns and forensic fingerprint detection were designed and successfully performed. Thus, the synthesized nanophosphor will have potential applications in different areas, such as security ink, forensic fingerprint detection and *in vitro* bioimaging.

Data availability

All the data are available from the corresponding authors upon request.

Conflicts of interest

There are no conflicts to declare.

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