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Enhanced visible and near infrared emissions *via* Ce^{3+} to Ln^{3+} energy transfer in Ln^{3+} -doped CeF_3 nanocrystals (Ln = Nd and Sm)†

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We report the enhancement of both visible and near infrared (NIR) emissions from Nd³+ ions via Ce³+ sensitization in colloidal nanocrystals for the first time. This is achieved in citrate capped Nd³+doped CeF₃ nanocrystals under ultraviolet (UV) irradiation (λ_{ex} = 282 nm). The lasing transition ($^4F_{3/2} \rightarrow ^4I_{11/2}$) at 1064 nm from Nd³+-doped CeF₃ nanocrystals has much higher emission intensity via Ce³+ ion sensitization compared to the direct excitation of Nd³+ ions. The nanocrystals were prepared using a simple microwave irradiation route. Moreover, the study has been extended to Sm³+-doped CeF₃ nanocrystals which show strong characteristic emissions of Sm³+ ions via energy transfer from Ce³+ ions. The energy transfer mechanism from Ce³+ to Nd³+ and Sm³+ ions is proposed.

1. Introduction

There is a surge in research interest towards developing lanthanide ($\rm Ln^{3+}$)-doped nanomaterials as they show sharp luminescence signals with longer excited state lifetimes (in the range of μ s to ms). In addition, $\rm Ln^{3+}$ ions show luminescence peaks over a wide electromagnetic spectrum. Particularly interesting are those emitting in the near-infrared (NIR) region *i.e.* the spectrum with the wavelength range of 700 to 2100 nm. NIR luminescence of lanthanide ions ($\rm Ln^{3+}$) finds applications in NIR LED technology, lasers, solar energy conversion, medical science and telecommunication. $\rm ^{1-4}$ For example, $\rm Ln^{3+}$ ions such as $\rm Er^{3+}$, $\rm Nd^{3+}$, $\rm Tm^{3+}$ and $\rm Ho^{3+}$ have characteristic emissions in the NIR region and can be used as active materials for developing optical amplifiers. $\rm ^{5-7}$ In addition, NIR emission is quite valuable for biological applications because

auto-fluorescence, deep penetration and being transparent to biological tissues.8-11 However, Ln3+ ions in aqueous media show very weak emission intensities owing to their low molar absorption coefficients (2–10 M⁻¹ cm⁻¹), which is attributed to both spin- and parity-forbidden 4f-4f transitions of Ln³⁺ ions.12-14 In addition, nonradiative transitions are very efficient in aqueous medium leading to further reduction of luminescence efficiency. One way to improve the luminescence efficiency is via an antenna effect, where typically an organic fluorophore possessing a high absorption coefficient is used as a sensitizer for Ln3+ ions. The organic fluorophore transfers the absorbed energy to Ln3+ ions leading to an enhanced luminescence quantum efficiency of Ln³⁺ ions. However, most of the reports on the antenna effect are restricted to Ln³⁺ complexes. 15,16 Moreover, organic molecules generally photobleach and are relatively less stable. On the other hand, Ce³⁺ ions can be used as a sensitizer as they possess a high absorbance coefficient (~10⁻¹⁸ cm²) due to allowed 4f-5d transitions. 17-20 The optical characteristics of Ce³⁺ ions for efficient energy transfer are mainly attributed to two reasons: broad emission leading to better overlapping with absorption bands of other Ln3+ ions and faster luminescence decay. 21-24 However, sensitization of luminescence via Ce3+ ions is mostly restricted to visible emission of Tb³⁺ ions and to some extent Dy³⁺ ions. ^{25,26} Recently, we have used Ce3+ ions for sensitizing Tm3+ ions to obtain single band blue emission from NaYF4 nanocrystals.27

of lower scattering from the body than visible photons, low

Our objective is to sensitize NIR emissions using Ce^{3^+} ions. Among NIR emitting Ln^{3^+} ions, Nd^{3^+} and Sm^{3^+} are interesting for the following reasons. For example, Nd^{3^+} ions show an important laser transition at 1064 nm (*e.g.* Nd^{3^+} -doped $Y_3Al_5O_{12}$). $^{28-30}$ In fact the 1064 nm is used for achieving 532 nm via second harmonic generation. Furthermore, this emission due to the transition from $^4F_{3/2} \rightarrow ^4I_{11/2}$ energy levels falls well in the second "human optical window" (1000–1350 nm). $^{31-35}$ Similarly, Sm^{3^+} ions show two emissions in this optical window (near 1020 and 1150 nm) in addition to a strong emission at 940 nm. Moreover, the emission of Nd^{3^+} shows remarkable thermal sensitivity leading to their use as

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sub-tissue thermal sensors.36-38 However, both Nd3+ ions and Sm3+ ions show sharp f-f absorption which are difficult to pump. 39-41 Although there are quite a few reports on Ce3+ to Nd³⁺ energy transfer, they are mostly restricted to a glass matrix. 42-46 In fact, to our knowledge there are no reports on Ce³⁺ sensitized NIR emissions from Nd³⁺ or Sm³⁺ ions in colloidal nanocrystals, particularly in aqueous milieu. 47,48 This is important as there is increasing demand for NIR emitting materials for biological imaging applications. Furthermore, colloidal nanocrystals can easily be coated or incorporated in sol-gel systems which is helpful for thin film device fabrication.

In this article, we report enhanced visible and NIR luminescence from Nd3+-doped CeF3 nanocrystals via Ce3+ sensitization. The lasing transition (${}^4F_{3/2} \rightarrow {}^4I_{11/2}$) at 1064 nm from Nd3+-doped CeF3 nanocrystals has shown emission strength about 3 times higher compared to that of the direct excitation of Nd³⁺ ions. Similarly, strong emissions in the NIR region are observed for Sm3+-doped CeF3 nanocrystals. We emphasize that all these are achieved from water and DMSO dispersible colloidal nanocrystals which can be useful for bioimaging applications.

Experimental section

2.1. Materials

Cerium nitrate [Ce(NO₃)₃, 99.98%], neodymium oxide [Nd₂O₃, 99.9%], samarium nitrate [Sm(NO₃)₃, 99.9%], trisodium citrate (>98%), sodium tetrafluoroborate (98%) and absolute ethanol were purchased from Sigma Aldrich. All chemicals were of analytical grade and used without further purification. Double distilled water was used throughout the synthesis and characterization.

2.2. Synthesis

Citrate functionalized Ln3+-doped CeF3 nanocrystals were prepared by a simple microwave assisted method. Briefly, 0.95 mmol of Ce(NO₃)₃ and 0.05 mmol of Nd(NO₃)₃ were taken in a 100 ml round bottom flask and completely dissolved in 15 ml of double distilled water. To this clear aqueous solution 1.5 mmol NaBF₄ and 4 mmol trisodium citrate (TSC) were added and stirred until complete dissolution. The mixture was magnetically stirred for 15 minutes at room temperature. Finally the mixture was transferred to a 30 ml vial, used for microwave synthesis. The synthesis was carried out using the Anton Parr 300 microwave reactor. The vial was tightly sealed with a Teflon cap and the reaction was carried out at 180 °C for 10 minutes and then cooled to room temperature. The product was collected by centrifugation and washed thrice with absolute ethanol. It should be noted that the microwave experiments were carried out in temperature control mode. Simultaneous gas jet cooling (3-5 bar) during microwave irradiation was performed by using compressed air (6 bar). All microwave experiments were carried out using magnetic stirring at a rate of 600 rpm. The same protocol was used for the

synthesis of citrate capped Sm³⁺-doped CeF₃ nanocrystals. [0.97 mmol of Ce(NO₃)₃ and 0.03 mmol of Sm(NO₃)₃ in 15 mL double distilled water.]

2.3. Characterization

Powder X-ray diffraction (PXRD) measurements were performed on a Rigaku-smartlab diffractometer with Cu Kα operating at 70 kV and 35 mA at a scanning rate of 1° min⁻¹ in the 2θ range from 20° to 80° . The samples were completely powdered and spread evenly on a quartz slide. TEM measurement was carried out using a high resolution FEG transmission electron microscope (JEOL, JEM 2100F) with a 200 keV electron source. Briefly, a drop of the CeF3 nanocrystals in water was taken on a strong carbon coated 300 mesh Cu grid and dried in air. The FT-IR spectra were obtained with a Perkin Elmer Spectrum RX1 spectrophotometer with the KBr disk technique in the range of 400-4000 cm⁻¹. Thermogravimetric analysis was performed using the Mettler Toledo TGA 851 instrument under a N₂ atmosphere at a heating rate of 10° min⁻¹. The photoluminescence measurements were performed with the Horiba Jobin Yvon Fluorolog. All the emission spectra were recorded using the steady state 450 W Xe lamp as the excitation source. The luminescence lifetime measurements were performed using the Horiba Jobin Yvon Fluorolog machine with a pulsed Xe source of 150 W.

3. Results and discussion

Phase and structure

The phase analysis of the Ln^{3+} -doped CeF_3 (Ln = Nd and Sm) nanocrystals was performed using powder X-ray diffraction (XRD) measurements. Fig. 1 shows the XRD pattern of the Nd³⁺-doped CeF₃ nanocrystals along with that of a standard pattern for bulk CeF₃. All the peaks are matched well with that of the standard CeF₃ (ICSD PDF Card no. 00-038-0452) suggesting the formation of a pure hexagonal phase. The

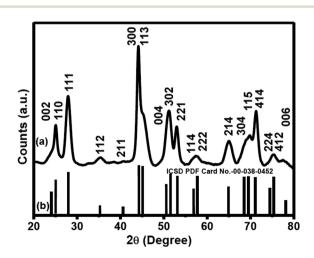


Fig. 1 Powder XRD patterns of (a) Nd³⁺-doped CeF₃ nanocrystals and (b) standard hexagonal CeF₃ crystals (ICSD PDF Card No-00-038-0452).

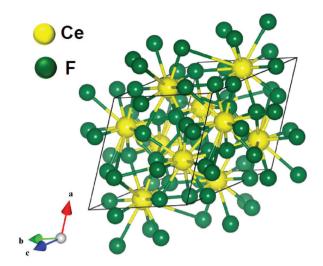


Fig. 2 Schematic presentation of the unit cell structure of ${\sf CeF}_3$ nanocrystals.

miller indices for each peak are shown above the corresponding peaks.

The average crystallite size is found to be 8.5 nm as calculated using the Debve-Scherrer equation, $t = (0.9\lambda/\beta \cos \theta)$, where t stands for average crystallite size, λ denotes the wavelength ($\lambda = 1.5418 \text{ Å}$) of incident X-ray, β denotes the corrected full width at half maximum (FWHM) and θ denotes the diffraction angle. Lattice parameters of Nd3+-doped CeF3 nanocrystals from XRD are found to be a = b = 7.1024, c = 7.2612 and $\alpha = \beta =$ 90°, $\gamma = 120^\circ$. The hexagonal phase CeF₃ nanocrystals adopt the same structure as LaF3, and the space group of these two crystals is P3c1. The highest point group of this structure is D_{3d}. In this structure, the anion ligand number is 12, i.e. each cation is surrounded by 12 anions. The cation sits at the center of an icosahedron. Twelve fluorides are close: four at the bottom corners of the icosahedron, four in the faces of the icosahedron, and four at the top corners of the icosahedron. The cation can be considered as 12 coordinate. The schematic of the unit cell crystal structure of hexagonal CeF3 obtained using the visualization for electronic and structural analysis (VESTA) program is shown in Fig. 2. The atomic coordinates (x, y and z) used for the calculations are used from the reported literature⁴⁹ and shown in Table S1 (see the ESI†).

3.2. Morphology analysis

The morphology of the citrate-functionalized Nd^{3+} -doped CeF_3 nanocrystals is obtained by transmission electron microscopy (TEM) as shown in Fig. 3. From the TEM image the formation of oval shaped nanocrystals is clear. The average aspect ratio of the Nd^{3+} -doped CeF_3 nanocrystals is found to be approximately 0.8 (length = 20 nm and breadth = 16 nm). For the semi-quantitative analysis of the elements present in the Nd^{3+} -doped CeF_3 nanocrystals energy-dispersive X-ray (EDX) analysis was performed. The EDX analysis spectrum of Nd^{3+} -doped CeF_3

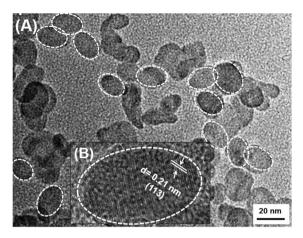


Fig. 3 TEM image of Nd^{3+} -doped CeF_3 nanocrystals and the inset shows the HR image of a nanocrystal. White color circles indicate the boundary of the nanocrystals.

nanocrystals are shown in Fig. S1 (see the ESI†). It confirms the presence of Ce, F, and Nd in the sample.

3.3. Surface functionalization

The high dispersibility of the citrate functionalized CeF₃ nanocrystals in water suggests the binding of citrate ions to the surface of the nanocrystals which is supported by the FTIR analysis. The FTIR spectra of citrate capped CeF₃ nanocrystals along with pure trisodium citrate molecules are shown in Fig. 4. For the free TSC, major peaks are observed near 3453, 2985, 1600 and 1399 cm⁻¹. The strong and broad stretching vibration band centered at 3448 cm⁻¹ is assigned to O–H in TSC and the peak at 2952 cm⁻¹ is attributed to the methylene (CH₂) stretching vibrations of the alkyl chains of TSC. The band at 1600 cm⁻¹ is assigned to the C—O asymmetric stretching vibration of the -COO⁻ group, and the band at 1399 cm⁻¹ is due to symmetric stretching vibrations of C–O in the -COO⁻ group of the TSC.⁵⁰ In the case of citrate capped Nd³⁺ doped

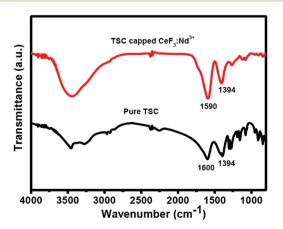


Fig. 4 FTIR spectra of citrate capped Nd^{3+} -doped CeF_3 nanocrystals and pure TSC molecules.

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CeF₃ nanocrystals, all the characteristic peaks for TSC molecules are observed, however the C=O stretching frequency is shifted towards a lower wavenumber (at 1590 cm⁻¹) which clearly indicates the binding of the TSC ligand onto the surface of the Nd³⁺ doped CeF₃ nanocrystals.

To further confirm the citrate functionalization onto the surface of CeF3 nanocrystals, TGA analysis was conducted. The TGA curves for both citrate capped CeF₃ nanocrystals and pure TSC are shown in Fig. S2, (see the ESI†). For the free TSC the major weight loss is noted from 250 °C due to the decomposition of TSC molecules. For the citrate functionalized CeF₃ nanocrystal, the onset of decomposition is shifted to the higher temperature (~275 °C) which further confirms that the citrate molecules are strongly attached to the surface of the CeF3 nanocrystals. The wt% of citrate molecules attached to the CeF3 is close to 3.12% as calculated from the weight loss from the TGA analysis. Further confirmation for the attachment of the citrate ligands to the nanocrystals comes from the high stability of the nanocrystals in water. The dispersion of the nanocrystals was relatively stable in water for more than 10 hours. The photoluminescence study suggests that the luminescence intensity of Nd3+ ions reduced by only ~30% after 10 hours. The digital images of the colloidal dispersion along with the corresponding emission spectra are shown in Fig. S3.†

3.4. Optical properties

Photoluminescence (PL) studies have been carried out for the colloidal 0.1 wt(%) Nd3+-doped CeF3 nanocrystals in water. Upon excitation at 282 nm, the nanocrystal dispersion shows visible and NIR emissions as shown in Fig. 5. The prominent band in the visible region is at 693 nm, which is assigned to the ${}^{2}I_{15/2} \rightarrow {}^{4}F_{7/2}$ transition. In addition, the nanocrystal dispersion shows characteristic NIR bands of Nd3+ ions at 1062

and 1339 nm in water, which are assigned to the ${}^4F_{3/2} \rightarrow {}^4I_{11/2}$ and ${}^4F_{3/2} \rightarrow {}^4I_{13/2}$ transitions, respectively. The most intense band at 1062 nm is potentially suitable for application in laser emission and telecommunication. The inset of Fig. 5 displays the excitation spectrum which shows an intense broad peak at 282 nm by monitoring the emission at 1062 nm. This peak is due to the 4f5d \rightarrow 5f electronic transition of Ce³⁺ ions. This confirms the energy transfer from Ce³⁺ to Nd³⁺ ions. To further verify the occurrence of energy transfer, we prepared Nd3+-doped (5 mol%) LaF3 nanocrystals using the same synthesis protocol. Upon excitation at 280 nm, no characteristic emission from Nd3+ ions is observed confirming the energy transfer from Ce³⁺ to Nd³⁺ in Nd³⁺-doped CeF₃ nanocrystals (see Fig. S4†). To understand the energy transfer efficiency, PL spectra of Nd3+-doped CeF3 nanocrystals were collected at direct excitation (514 nm) and 282 nm excitation. From Fig. 6, it is clear that upon 282 nm excitation the visible emission and NIR emission intensity increases by two and three times, respectively, compared to that of direct excitation. These results strongly suggest that efficient energy transfer occurs from Ce³⁺ to Nd³⁺ ions.

We have extended our study to check whether energy transfer from Ce³⁺ ions to Sm³⁺ ions is possible. The 3 mol(%) Sm3+-doped CeF3 nanocrystals were prepared using identical reaction conditions and characterized by XRD analysis. The XRD pattern suggests the formation of pure hexagonal phase CeF₃ nanocrystals as shown in Fig. S5.† The PL and excitation spectra of Sm3+ (3%)-doped CeF3 nanocrystals are shown in Fig. 7. Upon 280 nm excitation the dispersion of Sm³⁺-doped CeF₃ nanocrystals in DMSO shows intense peaks at 559, 593, 639 and 702 nm which are assigned to ${}^4G_{5/2} \rightarrow {}^6H_{5/2}$, ${}^4G_{5/2} \rightarrow$ $^6\mathrm{H}_{7/2},\,^4\mathrm{G}_{5/2} \rightarrow ^6\mathrm{H}_{9/2}$ and $^4\mathrm{G}_{5/2} \rightarrow ^6\mathrm{H}_{11/2}$ transitions, respectively. The ${}^4G_{5/2} \rightarrow {}^6H_{5/2}$ transition at 560 nm has a magnetic dipole character.⁵¹ The intensity ratio of $I(^4G_{5/2} \rightarrow {}^6H_{9/2})/I(^4G_{5/2} \rightarrow$ ⁶H_{5/2}) is 1.05 which indicates lower polarizability of the chemi-

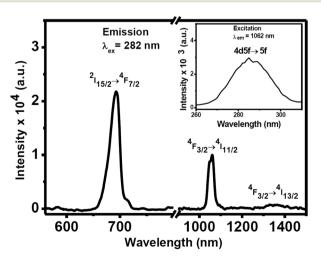


Fig. 5 PL spectrum of 5 mol(%) Nd³⁺-doped CeF₃ nanocrystals in water covering the visible to NIR region ($\lambda_{\rm exi}$ = 282 nm). The inset shows the excitation spectrum for the same nanocrystals (λ_{emi} =

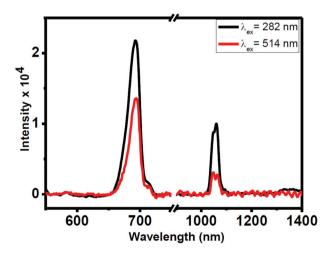


Fig. 6 PL spectra in the visible and NIR regions from Nd³⁺-doped CeF₃ nanocrystals via Ce3+ ion excitation (282 nm) and direct excitation (512 nm).

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Fig. 7 PL spectrum of 3 mol(%) $\rm Sm^{3+}$ -doped $\rm CeF_3$ nanocrystals in DMSO covering the visible to NIR region ($\lambda_{\rm ex} = 280$ nm). The inset shows the excitation spectrum for the same nanocrystals ($\lambda_{\rm em} = 939$ nm).

Wavelength (nm)

cal environment around the Sm3+ ions.52 In addition, the nanocrystals show strong NIR emission peaks at 939 nm, 1017 nm and 1152 nm which are ascribed to the ${}^4G_{5/2} \rightarrow {}^6F_{5/2}$, $^4\mathrm{G}_{5/2} o ^6\mathrm{F}_{7/2}$, and $^4\mathrm{G}_{5/2} o ^6\mathrm{F}_{9/2}$ transitions, respectively. These transitions are characteristics of Sm3+ ions. Among these peaks, 939 peaks are quite intense and they fall in the first "human optical window". It is quite clear from Fig. S6,† that upon 280 nm excitation, both visible and NIR emission intensities increase by two times compared to that of direct excitation (400 nm). We have performed some control experiments to test the effect of the concentrations of Nd3+ and Ce3+ ions on the emission intensity of the nanocrystals. There is an increase in the emission intensity up to 5 mol% doping for the Nd³⁺ ions and there upon a decrease is noted. Similarly, the optimum doping concentration for Sm3+-doped CeF3 is found to be 3 mol% (see Fig. S7†).

Enhancement of visible and NIR emissions for both Nd3+ and Sm³⁺ ions is achieved *via* energy transfer from Ce³⁺ ions. This is supported by the overlap between the emission spectrum of Ce³⁺ ions with the absorbance of Sm³⁺ and Nd³⁺ ions. The results are shown in Fig. S8.† The energy transfer efficiency between the donor (Ce3+) and acceptor (Nd3+/Sm3+) is evaluated using the equation $\eta = 1 - \tau_d/\tau_{d0}$. The average terms τ_d and τ_{d0} are denoted for the excited state lifetimes of the sensitizer in the presence and absence of the activator, respectively. The lifetimes of the sensitizer Ce³⁺ ions in the presence and absence of an emitter (i.e. Nd3+/Sm3+ ions) are calculated using Time Correlated Single Photon Counting (TCSPC). The lifetime values of Ce³⁺ ions in CeF₃, CeF₃:Nd³⁺ (5%) and CeF₃:Sm³⁺ (3%) nanocrystals are found to be 23 ns, 9.7 ns and 12 ns, respectively.⁵³ Lifetime decay curves are shown in Fig. S9 (see the ESI†). The calculated energy transfer efficiencies from Ce3+ to Nd3+ and Sm3+ are close to 57% and 48%, respectively. To understand the effect of Nd³⁺ concentration in CeF₃ on the energy transfer efficiency between Ce³⁺

and Nd³⁺, we have calculated the corresponding lifetimes of Ce³⁺ emissions. It is interesting to note that the energy transfer efficiency increases with the increase in the Nd concentration. The values are 53%, 55%, 57% and ~80% respectively, for 1, 3, 5 and 8 mol% Nd³⁺ doping in CeF₃ nanocrystals. Please note that the optimum luminescence efficiency of Nd³⁺ is 5 mol%. This suggests that though there is a higher energy transfer probability between Ce3+ to Nd3+ at a higher doping concentration, the cross relaxation between Nd3+-Nd3+ is higher leading to self-quenching of the luminescence. The lifetime decay curves are shown in Fig. S10.† Furthermore, we have measured the lifetimes of Sm³⁺ and Nd³⁺ ions in Sm³⁺ and Nd3+ doped CeF3 nanocrystals, respectively. The lifetime of Sm³⁺ ions is 741 µs when excited at 282 nm and emission was monitored at 599 nm. The lifetime of Nd³⁺ ions is 8 μs when excited at 282 nm and emission was monitored at 693 nm as shown in Fig. S11.† 53

3.5. Energy transfer mechanism

The proposed energy transfer mechanism between Ce³⁺ to Nd³⁺ ions and Sm³⁺ ions is schematically shown in Fig. 8. Upon 282 nm excitation, Ce3+ ions get excited from 4f1 to 4f⁰5d¹ levels. A radiative energy transfer occurs from the relaxed lowest 4f5d energy level of Ce³⁺ ions to the ²I_{15/2} energy level of Nd³⁺ ions followed by radiative transfer to the low lying ⁴F_{7/2} level of Nd³⁺ ions. Subsequently, energy transfer from ⁴F_{7/2} to ⁴F_{3/2} occurs nonradiatively. Radiative relaxation from ${}^4F_{3/2}$ levels to the ${}^4I_{11/2}$ and ${}^4I_{13/2}$ energy levels of Nd $^{3+}$ ions, lead to the 1064 nm and 1339 nm NIR emissions, respectively. Similarly, for Sm³⁺-doped CeF₃ nanocrystals, upon 280 nm excitation, Ce^{3+} ions are excited from the $4f^{0}5d^{1} \rightarrow 4f^{1}$ level. A radiative energy transfer occurs from the lowest 4f5d energy band of Ce³⁺ ions to the ⁴D_{1/2} energy level of Sm³⁺ ions followed by nonradiative transfer to the low lying 4G5/2 level of Sm³⁺ ions. Subsequent decays from ⁴G_{5/2} levels and ⁶F_{9/2} levels to the ${}^{6}H_{5/2}$, ${}^{6}H_{7/2}$, ${}^{6}H_{9/2}$, ${}^{6}H_{11/2}$, ${}^{6}F_{5/2}$, ${}^{6}F_{7/2}$ and ${}^{6}F_{9/2}$ Sm³⁺ ions, result in emissions in the visible and NIR regions.

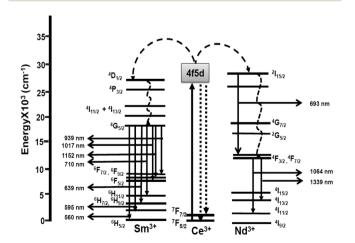


Fig. 8 Schematic of the proposed energy transfer mechanism from Ce^{3+} ions to Nd^{3+} and Sm^{3+} ions.

Conclusions 4.

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In conclusion, we have successfully synthesized hexagonal phase Ln³⁺ doped CeF₃ nanocrystals via a microwave assisted method. The morphology of the nanocrystals was oval shaped with an average aspect ratio of ~ 0.8 . The nanocrystals are functionalized with citrate molecules which render them highly water dispersible. In Nd³⁺ and Sm³⁺-doped CeF₃ nanocrystals, enhanced visible and near infrared (NIR) emissions were observed via Ce3+ ion sensitization upon ultraviolet (UV) irradiation (λ_{exi} = 280 nm). The energy transfer mechanism from Ce³⁺ to Nd³⁺ and Sm³⁺ ions is proposed. The strong NIR emissions from water dispersible nanocrystals are advantageous for bioimaging applications. In addition, they can easily be incorporated into polymers and other sol-gel matrices for fabrication devices telecommunications.

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