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Intense NIR emissions at 0.8 µm, 1.47 µm, and 1.53 µm from colloidal LiYbF₄:Ln³⁺ (Ln=Tm³⁺ and Er³⁺) nanocrystals

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We report on the synthesis of diamond shaped Ln³⁺-doped LiYbF₄ (Ln=Tm and Er) nanocrystals with flat edges via the thermal decomposition method. Strong near-infrared emissions at 0.8 µm, 1.47 µm and 1.53 µm are observed from colloidal dispersions of Tm³⁺-doped and Er³⁺-doped LiYbF₄ nanocrystals, respectively under 0.98 µm diode laser excitation. The NIR emission intensities for Tm³⁺-doped and Er³⁺-doped LiYbF₄ nanocrystals are comparable with those of the sodium counterpart NaYbF₄ suggesting that LiYbF₄ is also an excellent host matrix for lanthanide ions to obtain strong NIR emissions in colloidal solutions of LiYbF₄ (Tm³⁺ or Er³⁺) nanocrystals.

1. Introduction

Upconverting nanomaterials which are able to convert lower energy radiation (near-infrared) to higher energy radiation (ultraviolet (UV) or visible) by absorbing one or more low energy photons are getting much attention recently owing to their potential use in a wide range of applications from optoelectronic devices to bioimaging.1-15 The upconversion (UC) process is largely exhibited by lanthanide (Ln³⁺) ions and generally occurs by three different mechanisms; energy transfer upconversion (ETU), excited state absorption (ESA) and photon avalanche (PA).16-18 Among these mechanisms, ETU is predominantly observed in colloidal nanocrystals particularly in Yb³⁺ ions co-doped materials. Due to higher absorption coefficient of the Yb³⁺ ion compared to other Ln³⁺ ions, it is used as a sensitizer. Moreover, excitation wavelength of the laser diode (0.98 µm) may be used to excite the Yb³⁺ ions.19,20 Among the available matrices for Ln³⁺ ions, fluorides are considered as ideal hosts due to their low phonon energy which reduces the nonradiative relaxations.21-29

There are several reports on upconverting Ln³⁺-doped fluoride nanoparticles. One of the major interests of UC nanomaterials is in bioimaging since excitation at 0.98 µm allows deeper penetration of light in tissues, reduces autofluorescence and increases image contrast.30-32 Particularly interesting are materials where the emission peaks are also in the NIR region. A number of reports can be found on NIR to NIR upconversion emission. For example, Prasad’s group have shown NIR to NIR upconversion emission from ultrasmall Yb³⁺/Tm³⁺-doped NaYF₄ nanocrystals. By increasing the Yb³⁺ ions concentration from 20 to 100% a great enhancement (43 times) of NIR to NIR UC emission was observed.33 The same group have also shown NIR to NIR downconversion photoluminescence from core/shell NaGdF₄:Nd³⁺/NaGdF₄ nanocrystals.34 In another study, they have shown NIR upconversion emission from core/shell NaYbF₄/CaF₂ nanocrystals which was used in high contrast deep tissue bioimaging.35 However, the majority of the above mentioned studies concentrate on the 0.8 µm emission from Tm³⁺ or Nd³⁺ ions. NIR emissions particularly near 1.5 µm (1.53 µm and 1.47 µm) are interesting for telecommunication applications. These emissions have been reported in solid state materials however, only few reports are available on colloidal systems. This is probably due to the efficient quenching of these emissions by nonradiative relaxations. For example, 1.47 µm Stokes emission of Tm³⁺ ions has been reported for LaF₃:Tm³⁺/LaF₃ core-shell nanoparticles.6 We have reported similar ~1.46 µm emission from Yb³⁺/Tm³⁺ co-doped LiYF₄ nanocrystals under 0.98 µm laser excitation.37 However, to produce dispersible nanocrystals exhibiting strong NIR emissions at wavelengths above 0.8 µm remains a challenge. The advantage of colloidal nanocrystals would be the uniform coating over any surfaces and facile integration into thin film devices.

In this article, we report the synthesis of colloidal Ln³⁺-doped LiYbF₄ nanocrystals (Ln=Tm³⁺ and Er³⁺) stabilized by oleate ligands and produced via the thermal decomposition method (see experimental section for details). NIR (0.98 µm) to NIR (0.8 µm) emission via upconversion process was achieved by doping Tm³⁺ ions in the host matrix, LiYbF₄. Moreover, Tm³⁺-doped and Er³⁺-doped LiYbF₄ nanocrystals show strong 1.46 µm and 1.53 µm Stokes emissions via upconversion
respectively, which are important wavelengths for application in telecommunication.

2. Experimental

2.1 Materials and methods

All the chemicals used in this work, thulium oxide (Tm₂O₃, 99.99%), erbium oxide (Er₂O₃, 99.99%), ytterbium oxide (Yb₂O₃, 99.99%), trifluoroacetic acid (CF₃COOH, 99%), oleic acid (90%), 1-octadecene (90%) and lithium trifluoroacetate (CF₃COOLi, 99.99%), sodium trifluoroacetate (CF₃COONa, 99.99%), absolute ethanol were purchased from Sigma Aldrich. All the materials were used without further purification.

2.2 Synthesis of nanocrystals

Ln³⁺-doped LiYbF₄ nanocrystals were prepared via the thermal decomposition method using oleic acid as capping agent and 1-octadecene as high boiling point solvent. Briefly, lanthanide trifluoroacetates were first prepared by refluxing stoichiometric amounts of corresponding lanthanide oxides with 1:1 trifluoroacetic acid and water at 85°C and then evaporated at 65°C to dryness. CF₃COOLi, oleic acid (20 mL) and 1-octadecene (20 mL) were added to dried precursors and the resulting mixture was heated to 120°C under vacuum. After 15 minutes, the temperature of the mixture was raised to 310°C under an argon flow for 1 h. The mixture was cooled to room temperature and the nanocrystals were precipitated with absolute ethanol. The nanocrystals were separated by centrifugation and further purified by dispersing them in hexane followed by precipitation again with absolute ethanol. A 1 wt% colloidal dispersion was prepared by dispersing approximately 100 mg of the nanocrystals in 10 mL of toluene.

2.3 Characterization techniques

Powder X-ray diffraction (PXRD): Analysis of the phase of the as prepared Ln³⁺-doped LiYbF₄ (Ln=Tm or Er) nanocrystals was carried out by powder X-ray diffraction (XRD) measurements, using a Rigaku-smartlab diffractometer with Cu Kα operating at 200 kV and 45 mA at a scanning rate of 1° min⁻¹ in the 2θ range from 15° to 90°. The samples were spread evenly on a quartz slide.

Transmission electron microscopy (TEM): The morphology of the nanocrystals were characterized by transmission electron microscopy (TEM), using a FEI (Czech Republic), FP5018/40 TECHNAI G² SPIRIT BioTWIN transmission electron microscope operated at 120 kV. Prior to analysis, a 10 mg sample was dispersed in 10 ml of toluene to make a 0.1 wt% solution. A drop of the toluene dispersion was evaporated on a 300 mesh copper grid.

Scanning electron microscopy (SEM): Scanning electron microscopy images were taken using a ZEISS (SUPRA) instrument. Prior to loading of the samples into the chamber, they were coated with a thin film of gold-palladium in order to avoid charging effects.

Fourier transform infrared (FTIR) spectroscopy: The FTIR spectra were recorded using a Perkin Elmer Spectrum RX1 spectrophotometer with the KBr disk technique in the range of 400-4000 cm⁻¹. The FTIR spectra of the samples was recorded using 10 mg of the samples mixed with 200 mg of KBr to produce the pellets.

Luminescence studies: The upconversion emission (UC) spectra were obtained by exciting a 1 wt (%) solution (nanocrystals dispersed in toluene) using a 0.98 µm diode laser (RGB Lase LLC), which was coupled with a fibre with a core diameter of 100 µm. The output signal was measured with a Jobin Yvon Fluoromax-4 spectrometer. The 1.47 µm emissions were collected using a Jobin Yvon Fluorolog system under 0.98 µm CW diode laser excitation and the signal was detected using a NIR PMT module detector (HAMAMATSU, H10330A series).

3. Results and discussion

Powder X-ray diffraction (XRD) pattern of the 1 mol(%) Tm³⁺-doped LiYbF₄ nanocrystals and the standard pattern for LiYbF₄ crystals are shown in Fig. 1. The XRD pattern of LiYbF₄ nanocrystals is in agreement with the standard pattern of tetragonal LiYbF₄ crystals (ICSD PDF Card No. 01-071-1211) suggesting the formation of pure tetragonal phase nanocrystals. Similarly, the XRD patterns of 2 mol(%) Er³⁺-doped LiYbF₄ nanocrystals matches with that of standard pattern of LiYbF₄ crystals (see Fig. S1, ESI†).

![Fig. 1 XRD patterns of (a) 1 mol(%) Tm³⁺-doped LiYbF₄ nanocrystals and (b) standard bulk LiYbF₄ (ICSD PDF Card No. 01-071-1211).](image-url)

The LiYbF₄ nanocrystals crystallize in tetragonal phase with I₄₁/a space group. The lattice constants of tetragonal LiYbF₄ nanocrystals were found to be a=b=5.1005Å, c=10.5564Å. These values match well with the standard values a=b=5.1335Å, c=10.5880Å for bulk LiYbF₄. The slight increase in the ‘a’ and ‘b’ values could be due to the larger ionic radii of the dopant ions, Tm³⁺ (r=0.994Å) compared to the Yb³⁺ ions (r=0.985Å). The structure of the tetragonal unit cell of LiYbF₄ is shown in Fig. 2, which is drawn using the Visualization for Electronic and Structural Analysis (VESTA)
program using the lattice parameters obtained from the XRD diffraction measurements and the atomic coordinates from the literature. Coordination of Yb\(^{3+}\) ions with F\(^-\) ions are also shown in the unit cell structure. The Yb\(^{3+}\) ions are surrounded by eight fluoride ions that form the edges of a slightly distorted dodecahedron.\(^{39,40}\)

![Space group I41/a](Image)

**Fig. 2** Schematic representation of the tetragonal unit cell structure of LiYbF\(_4\) nanocrystals. The coordination of Yb\(^{3+}\) ions is also shown.

Morphological analyses of the as synthesized Tm\(^{3+}\)-doped LiYbF\(_4\) nanocrystals have been performed using high resolution transmission electron microscopy (HRTEM) and SEM. The HRTEM image of the Tm\(^{3+}\)-doped LiYbF\(_4\) nanocrystals are shown in Fig. 3 and in Fig. S2. It is important to note that the shape of the 1 mol(%) Tm\(^{3+}\)-doped LiYbF\(_4\) nanocrystals show slightly flattened edges of the perfect diamond with an average aspect ratio (length/breadth) of 1.4 as shown in the histogram (Fig. 3B). We emphasize that in TEM analysis we observed few nanocrystals with larger size (~80 nm) with similar morphology. However, the number of larger particles is very low. The observed shape is slightly different from that reported for LiYF\(_4\) nanocrystals by Mahalingam et al.\(^{37}\)

![TEM image of Tm\(^{3+}\)-doped LiYbF\(_4\) nanocrystals](Image)

**Fig 3** (A) TEM image of Tm\(^{3+}\)-doped LiYbF\(_4\) nanocrystals, and (B) particle size (aspect ratio) distribution.

We postulate that this could be due to the difference in the ionic radii of the Ln\(^{3+}\) ions. In the case of Yb\(^{3+}/\)Tm\(^{3+}\)-doped LiYF\(_4\) nanocrystals, the ionic radius of the Y\(^{3+}\) ion is 1.019 Å, which is larger than the ionic radii of the dopant ions Tm\(^{3+}\) (r=0.994 Å) and Yb\(^{3+}\) (r=0.985 Å). Whereas, in the case of LiYbF\(_4\) the ionic size of Yb\(^{3+}\) is smaller than the Tm\(^{3+}\) (r=0.994 Å) or Er\(^{3+}\) (r=1.004 Å) ions. This causes a slight expansion of the lattice that is reflected in the lattice parameters (vide supra) and such expansion may result in a slight distortion at the tip of the diamond, as they possess higher surface energy. The observed, slightly flattened diamond shape morphology of the nanocrystals is further supported by scanning electron microscopy (SEM) measurement. The SEM image of the 1 mol(%) Tm\(^{3+}\)-doped LiYbF\(_4\) nanocrystals is shown in Fig. S3 (see ESI†).

The oleate capping of the surface of the nanocrystals is confirmed by Fourier Transform Infra-red (FTIR) measurements. The FTIR spectra of the oleate capped Tm\(^{3+}\)-doped LiYbF\(_4\) nanocrystals and pure oleic acid are shown in Fig. S4 (see ESI†). It is clear from the spectra that the peak at 1715 cm\(^{-1}\) observed in free oleic acid shifts to the lower wavenumber (1545 cm\(^{-1}\)) for the oleate capped nanocrystals indicating that –COO\(^-\) groups of oleic acid are bound to the surface of the nanocrystals.\(^{41}\) The long aliphatic chain of oleic acid renders the nanocrystals dispersible in hydrophobic solvents like hexane, toluene, etc.

The upconversion (UC) emission spectrum of the 1wt% toluene dispersion of the LiYbF\(_4\):Tm\(^{3+}\) (1%) nanocrystals under 0.98 μm CW diode laser excitation is shown in Fig. 4. A strong emission peak around 0.8 μm corresponding to the \(^{3}I_{4}→^{3}H_{6}\) transition is clearly visible in the UC emission spectrum. Along with the 0.8 μm peak three peaks at 0.478 μm, 0.65 μm and 0.7 μm are observed whose emission intensities are relatively weak in comparison to the 0.8 μm peak emission intensity. The corresponding peak assignments are shown in the Fig. 4. This observation is different from that of the Yb\(^{3+}/\)Tm\(^{3+}\)-doped LiYF\(_4\) nanocrystals.\(^{10}\) Generally, in Yb\(^{3+}/\)Tm\(^{3+}\) co-doped systems such as, LiYF\(_4\):Yb\(^{3+}/\)Tm\(^{3+}\) and NaYF\(_4\):Yb\(^{3+}/\)Tm\(^{3+}\) the blue emission is quite intense and nearly the same as the NIR emission. A comparison of the UC emission spectra (shown in Fig. 5) of Yb\(^{3+}/\)Tm\(^{3+}\) (20%)/Tm\(^{3+}\) (1%) nanocrystals under identical conditions show a high NIR to blue emission intensity ratio for the Tm\(^{3+}\)-doped LiYbF\(_4\) nanocrystals.

![UC emission spectrum of 1 mol(%) Tm\(^{3+}\)-doped LiYbF\(_4\) nanocrystals](Image)

**Fig 4** The UC emission spectrum of 1 mol(%) Tm\(^{3+}\)-doped LiYbF\(_4\) nanocrystals under 0.98 μm excitation. Inset shows logarithmic plot of UC emission intensity versus laser power for the 0.8 μm peak.

To understand the reason for the observed differences and to ascertain the number of photons involved in the UC process we performed power dependent UC emission studies. The UC emission intensity(I) is proportional to the laser power (P), raised to the n where n is the number of incident photons.
propose the following two CR mechanisms occurring in the cross relaxations processes are denoted as CR1 and CR2. These CR processes lead to the population of the visible emissions might be due to back transfer of the energy to the Yb$^{3+}$ ions. However, if back energy transfer alone is occurring then it should affect the 800 nm emission more compared to other emissions as the $^3H_4$ level is closer in energy. So we believe there is additional cross relaxations (CR) occurring along with the back energy transfer. This alone cannot explain the observed results. We propose the following two CR mechanisms occurring in the materials studied; $[^1G_4, \ 1^H_6 \rightarrow 2^F_{2,4,5} ]$ and $[^1G_4, \ 3^H_4 \rightarrow 3^H_6, \ 3^H_5 ]$. These CR processes lead to the population of the $^2F_{2,4,5}$ and $^3H_{6,5}$ levels. Thus the emission intensities of the transition (700 nm and 800 nm) originating from these levels are not affected to a large extent whereas the transitions originating from $^1G_4$ level are affected.

Similar CR processes have been reported for Tm$^{3+}$-doped tellurite glasses. A schematic of the possible energy transfer mechanism between Yb$^{3+}$ and Tm$^{3+}$ ions along with CR processes are shown in Fig. 6.

To understand the influence of Tm$^{3+}$ ions concentration on the UC emission intensity of the LiYbF$_4$ nanocrystals and to determine the optimal concentration of Tm$^{3+}$ ions in LiYbF$_4$ matrix, a series of samples with 0.5, 0.75, 1.0 and 1.5 mol% Tm$^{3+}$ ions were prepared. As shown in Fig. 7 the intensity of the NIR emission (0.8 µm) is highest for 1.0% Tm$^{3+}$-doped LiYbF$_4$ nanocrystals. A plot of the integrated area of UC emission spectra as a function of Tm$^{3+}$ ions concentration are shown in the inset of Fig. 7. It is also evident from the spectra that the change in UC emission intensity with concentration of Tm$^{3+}$ ions is not the same for the emission peaks at 0.478 µm, 0.65 µm and 0.8 µm.

We have extended the study to Er$^{3+}$-doped LiYbF$_4$ nanocrystals. The UC emission spectrum from a colloidal dispersion of 2 mol(%) Er$^{3+}$-doped LiYbF$_4$ nanocrystals is shown in Fig. 8. The UC emission spectrum shows two peaks at 0.52 and 0.54 µm, which are assigned to the $^3H_{11/2} \rightarrow ^1I_{15/2}$ and $^5S_{3/2} \rightarrow ^1I_{15/2}$ transitions, respectively. It is interesting to note that both transitions show approximately equal intensity, though the energy difference between the two levels is only 760 cm$^{-1}$ and can easily be matched with few phonon vibrations. We assume that the same intensity of these two peaks may be due to thermal equilibration of the population leading to equal distribution. However, the green emission peaks are less intense compared to red peak at 0.65 µm, which corresponds to $^4F_{9/2} \rightarrow ^4I_{15/2}$ transitions. To ascertain that this is not due to weak green UC emission from LiYbF$_4$:Er$^{3+}$ (2%) nanocrystals we have compared UC emission spectra of both Yb$^{3+}$ (20%)/Er$^{3+}$ (2%)-doped LiYF$_4$ and Er$^{3+}$ (2%)-doped LiYbF$_4$ nanocrystals under identical condition (Fig. S5, see ESI†). From the spectra it is clear that UC emission intensity of the green peak is lower than the red emission in LiYbF$_4$ compared to that of Y$^{3+}$ counterpart.

![Fig. 6 Schematic energy level diagram with predicted energy transfer mechanism between Yb$^{3+}$ and Tm$^{3+}$ ions in LiYbF$_4$ nanocrystals. The two cross relaxations processes are denoted as CR1 and CR2.](image)

![Fig. 5 The upconversion emission spectra of LiYbF$_4$:Yb$^{3+}$ (20%)/Tm$^{3+}$ (1%) (red trace) and LiYbF$_4$:Tm$^{3+}$ (1%) (black trace) nanocrystal under 0.98 µm excitation with a laser power density 70W/cm$^2$.](image)

![Fig. 7 The upconversion emission spectra of Tm$^{3+}$-doped LiYbF$_4$ nanocrystal as a function of Tm$^{3+}$ ions concentration under 0.98 µm diode laser with a laser power 70W/cm$^2$. Inset shows the UC emission intensity as a function of Tm$^{3+}$ ions concentration.](image)
It is already established that, at high levels of doping of donor Yb$^{3+}$ ions, some of those Yb$^{3+}$ ions act as quenchers which induce a quenching effect via Er$^{3+}$-Yb$^{3+}$ back transfer. This is evident in the UC of the Er$^{3+}$(2%)-doped LiYbF$_4$ nanocrystals where the overall UC emission intensity is lower than that of Yb$^{3+}$(20%)/Er$^{3+}$(2%)-doped LiYF$_4$ nanocrystals (see Fig. S5, ESI†). Furthermore, the lifetime of Er$^{3+}$ ions in the Er$^{3+}$(2%)-doped LiYbF$_4$ nanocrystals is lower than that of the Yb$^{3+}$(20%)/Er$^{3+}$(2%)-doped LiYF$_4$ nanocrystals which also suggest the back transfer. The corresponding decay curves were measured under 0.488 µm direct excitation of Er$^{3+}$ ions (see Fig. S6, ESI†). However, if back energy transfer alone occurs then it should be more probable from red emitting state ($^4$F$_{9/2}$) as this level is closer in energy with respect to excited Yb$^{3+}$ level ($^2$F$_{5/2}$) in comparison to the green emitting levels ($^2$H$_{11/2}$ and $^4$S$_{5/2}$). Moreover, the intensity of the red emission is not affected to any great extent. As back energy transfer is quite probable, there must be additional feedback system(s) operating in the material preferentially populating the red emitting level. Thus, we proposed the cross-relaxation mechanism occurring between Yb$^{3+}$ and Er$^{3+}$ ions, which is quite possible since there is a higher concentration of Yb$^{3+}$ ions in the matrix. The possible energy transfer mechanisms between Yb$^{3+}$ and Er$^{3+}$ ions are shown in Fig. S7 (see ESI†). In this mechanism, the Yb$^{3+}$ ions act as sensitizers and Er$^{3+}$ ions as activator in the upconversion process. Under 0.98 µm laser excitation electrons from the ground state, $^2$F$_{5/2}$, of Yb$^{3+}$ are promoted to the excited state, $^2$F$_{7/2}$, followed by the transfer of energy from the $^2$F$_{5/2}$ level of Yb$^{3+}$ to the $^4$I$_{11/2}$ level of Er$^{3+}$. Through a second energy transfer from the $^2$F$_{5/2}$ level of Yb$^{3+}$ to the $^4$I$_{11/2}$ level of Er$^{3+}$ the electrons are promoted to the $^4$F$_{7/2}$ level (Er$^{3+}$). The electrons in the excited state decay non-radiatively to $^2$H$_{11/2}$, $^4$S$_{5/2}$ and $^4$F$_{02}$ energy levels and then radiatively decay to the ground state ($^4$I$_{15/2}$) of Er$^{3+}$ ions giving rise to green and red emissions, respectively. Along with these processes the suggested cross relaxations and the back energy transfer occur to selectively depopulate the green emitting levels (vide supra).

The optical study of Ln$^{3+}$-doped LiYbF$_4$ (Ln=Tm$^{3+}$ or Er$^{3+}$) nanocrystals was extended to the telecommunication window (1.46-1.54 µm). Interestingly, under 0.98 µm laser excitation a Stokes emission peak around 1.47 µm is observed from the 1 wt%(%) colloidal Tm$^{3+}$-doped LiYbF$_4$ nanocrystals. The 1.47 µm emission is assigned to $^3$H$_4$$\rightarrow$$^1$F$_4$ transitions, which is a very important wavelength as it falls in the S-band (1.46-1.54 µm) region of optical telecommunication. Similarly, an intense near-infrared luminescence peak close to 1.53 µm (corresponding to $^4$I$_{11/2}$$\rightarrow$$^4$F$_{15/2}$ transition) is observed from the 2 mol (%) Er$^{3+}$-doped LiYbF$_4$ nanocrystals. The NIR emission spectra of Tm$^{3+}$-doped and Er$^{3+}$-doped LiYbF$_4$ nanocrystals are shown in Fig. 9A and 9B, respectively. It is reasonable to assume that the 1.47 µm emission from Tm$^{3+}$ ions occurs via a two photon process as the emitting level ($^3$H$_4$) is higher in energy compared to $^2$F$_{5/2}$ level of Yb$^{3+}$ ions.37 Whereas, the NIR emission observed at the 1.53 µm for Er$^{3+}$ ions due to $^4$I$_{11/2}$$\rightarrow$$^4$F$_{15/2}$ transition may occur via a single photon process. The logarithmic plots of intensity vs. laser power for Tm$^{3+}$-doped (1.47 µm) and Er$^{3+}$-doped (1.53 µm) LiYbF$_4$ nanocrystals are shown in Fig. S8 and Fig. S9, respectively, (see ESI†). Linear fitting of these two curves led to the slope values 1.37 and 0.98 respectively for 1.47 µm (Tm$^{3+}$) and 1.53 µm (Er$^{3+}$) peaks.
4. Conclusions

In summary, we have synthesized Ln$^{3+}$-doped LiYbF$_4$ (Ln=Tm$^{3+}$ and Er$^{3+}$) nanocrystals via the thermal decomposition method. The nanocrystals are diamond shaped and slightly flattened at the edges. Strong NIR (0.8 µm) emission compared to visible emissions was observed from the colloidal dispersion of the 1 mol(%) Tm$^{3+}$-doped LiYbF$_4$ nanocrystals under excitation at 0.98 µm diode laser. We have proposed a cross relaxation mechanism for the selective quenching of the visible emission over the NIR emission. Moreover, Stokes emissions via upconversion process around 1.47 µm and 1.53 µm were observed respectively from Tm$^{3+}$-doped and Er$^{3+}$-doped LiYbF$_4$ nanocrystals which can find applications in telecommunication in addition to their use in bioimaging applications.

Acknowledgements

VM thanks Council of Scientific and Industrial Research (CSIR), India and IISER-Kolkata for financial support. SS thanks to UGC, India for his fellowship. JAC is a Concordia University Research Chair in Nanoscience and is grateful to Concordia University and NSERC for financial support of his research.

Notes and references

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†Electronic Supplementary Information (ESI) available: [PXRD pattern, SEM image, FTIR spectra, UC emission spectra, lifetime decay curves and UC energy transfer mechanism]. See DOI: 10.1039/b000000x/


5 T. Yang, Y. Sun, Q. Liu, W. Feng, P. Yang, and F. Li, *Biomaterials*, 2012, **33**, 3733-3742.


