Multicolor light emitters based on energy exchange between Tb and Eu ions co-doped into ultrasmall β-NaYF₄ nanocrystals†

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Multicolor emission is reported from ultrasmall (<10 nm) β-NaYF₄:Eu,Tb nanocrystals depending on the excitation wavelength or emission detection delay time. Detailed optical investigations of three samples (NaYF₄:Eu, NaYF₄:Tb and NaYF₄:Eu,Tb) obtained by a co-thermolysis method have been carried out. Photoluminescence, photoluminescence excitation and emission decay time obtained at different excitation wavelengths have been measured. Excitation mechanisms of Eu and Tb ions have been explained based on the experimental results and calculations using Judd–Ofelt theory. It has been shown that efficient energy transfer from Tb to Eu ions accounts for the efficient red emission of NaYF₄:Tb,Eu nanocrystals.

Introduction

Inorganic nanocrystals (NCs) doped with rare earth ions have potential applications in many modern optoelectronic devices. Nanosized dispersible phosphors have sharp and stable lanthanide emission suitable for use in devices such as flexible displays. Some recent progress in medical diagnostics, as well as in the study of biological systems,1,2 can be attributed to developments in optical probes. The superior photostability (no blinking or fading) and biocompatibility3 of nanophosphors make them potentially better materials than organic dyes and even many semiconducting nanoparticles. Organic fluorescent dyes can bleach during imaging whilst semiconducting nanoparticles can exhibit optical blinking4 and are in some cases toxic.5

Active research on nanosized lanthanide-doped phosphors started more than a decade ago6 and since then, significant advances have been made in the preparation and understanding of relations between their luminescent characteristics and resulting morphologies. More recently, co-doping of such matrices with two or more ions has been studied with NaYF₄ as the host matrix. Most of these materials are designed either to use photon cutting phenomena or to up-convert the IR light to higher energy. Only few reports exist (Y₂O₃:Tb,Eu) a dealing with Tb and Eu co-doped nanophosphors that emit in the visible region of the electromagnetic spectrum which from the application point of view is still the most useful/used spectral range especially in biology and medicine. Additionally, in many cases, the NCs are in the range of tens of nanometres strongly limiting their utility in many biomedical applications. Structural properties of such systems have been discussed in detail,9–11 however, a detailed understanding of their emission and excitation properties is still poorly understood. In general, the mechanisms responsible for the final emission efficiency can be very complicated. For example, when nanophosphors are co-doped with Eu and Tb, a strong energy transfer is expected from Tb⁶⁺ to Eu³⁺ ions.7 As the energy levels of lanthanide ions match perfectly, energy transfer is highly efficient and should be favored over light emitting decay.12 Moreover, weak back energy transfer from Eu⁰⁺ to Tb³⁺ is also expected.8,12

Herein, we will initially discuss in detail the interaction between Tb and Eu ions when both are introduced into a NaYF₄ matrix (~6 to 8 nm in diameter) of high crystal quality. In the later part, we will propose the use of such materials as multicolor labels where color selectivity can be obtained by changing delay time of emission or excitation wavelength.

Experimental details

Sodium trifluoroacetate Na(CF₃COO) (98%), yttrium(III) trifluoroacetate hydrate Y(CF₃COO)₃·xH₂O (99%), europium(III)
trifluoroacetate trihydrate Eu(CF<sub>3</sub>COO)<sub>3</sub>·3H<sub>2</sub>O (98%) and tri-octylphosphine oxide (TOPO, 90%) were purchase from Sigma Aldrich Ltd, UK and used as received without any purification.

**Synthesis of NaYF<sub>4</sub>:Eu<sup>3+</sup> nanocrystals**

The synthetic method for the preparation of β-NaYF<sub>4</sub>:Eu<sup>3+</sup> NCs was similar to the single step co-thermolysis method presented in our previous paper<sup>13</sup> as originally proposed by Shan et al.<sup>14</sup> In general, a mixture of 1.25 mmol Na(CF<sub>3</sub>COO), 0.485 mmol Y(CF<sub>3</sub>COO)<sub>3</sub> and 0.039 mmol Eu(CF<sub>3</sub>COO)<sub>3</sub> in 10 g TOPO was degassed at 120 °C under stirring. After 30 min, the reaction was purged with N<sub>2</sub> and the reaction temperature was increased to 350 °C. After 1 h, the reaction was cooled to 70 °C and excess ethanol was added to precipitate the nanoparticles. The resulting material was collected by centrifugation and excess TOPO was removed by washing with ethanol.

**Synthesis of NaYF<sub>4</sub>:Tb<sup>3+</sup> (5%) nanocrystals**

To prepare β-NaYF<sub>4</sub>:Tb<sup>3+</sup> (5%) NCs, 1.25 mmol Na(CF<sub>3</sub>COO), 0.485 mmol Y(CF<sub>3</sub>COO)<sub>3</sub>, 0.039 mmol Tb(CF<sub>3</sub>COO)<sub>3</sub> and TOPO (10 g) were loaded into a three neck flask. The experimental procedure and growth conditions were similar to those of NaYF<sub>4</sub>:Eu<sup>3+</sup> (5%) NCs.

**Synthesis of co-doped NaYF<sub>4</sub>:Eu<sup>3+</sup>,Tb<sup>3+</sup> (5%) nanocrystals**

To prepare co-doped β-NaYF<sub>4</sub>:Eu<sup>3+</sup>,Tb<sup>3+</sup> (5%) NCs the precursors of both Eu (0.039 mmol Eu(CF<sub>3</sub>COO)<sub>3</sub>) and Tb (0.039 mmol Tb(CF<sub>3</sub>COO)<sub>3</sub>) were loaded into the three neck flask. The experimental procedure and growth conditions were similar to those of NaYF<sub>4</sub>:Eu<sup>3+</sup> (5%) NCs.

**Characterization.** Samples for transmission electron microscope (TEM) experiment were prepared by evaporating a dilute toluene solution of the nanoparticles onto carbon coated copper grids (Cu-300HD, Pacific Grid Tech) and a FEI Titan Super Twin was used to obtain TEM images of the nanoparticles.

X-Ray powder diffraction (p-XRD) patterns were obtained using a Bruker D8 AXE diffractometer (Cu-Kα) using a Bruker D8 AXE diffractometer (Cu-Kα). The nanoparticles were dispersed on the sample holder using toluene. The X-ray powder diffraction (XRD) experiment was performed at room temperature using Cu-Kα radiation (λ=1.54 Å). The XRD pattern was recorded in a 2θ range of 10–90° with a step size of 0.02° and a scan rate of 0.02° per second. The p-XRD results were analyzed using the Scherrer equation to calculate the crystallite size.

**Results**

The doping of NaYF<sub>4</sub> NCs with Eu, Tb and Eu,Tb ions has been successfully achieved by co-thermolysis of metal acetates in TOPO. XRD data (see ESI†) of all NaYF<sub>4</sub> samples have been compared to reflections of the hexagonal NaYF<sub>4</sub> lattice standard (ICDD no: 28-1192). Obtained agreement of the diffraction peak positions with the reference indicates that NCs are of the pure hexagonal phase. The particle size was calculated from the p-XRD results using the Scherrer equation. The diameters of β-NaYF<sub>4</sub>:Eu, β-NaYF<sub>4</sub>:Tb and β-NaYF<sub>4</sub>:Tb,Eu were determined: 8.2 ± 0.5 nm, 6.3 ± 0.7 nm and 6.4 ± 0.7 nm, respectively. A decrease in NC diameter is clearly evident for the Tb doped samples.

Fig. 1 shows TEM and HR-TEM images of all three samples at two different magnifications. It is clear that the NCs are monodispersed and have close to spherical morphologies. It can be seen (Fig. 2(a) and (b)) that average diameter of β-NaYF<sub>4</sub>: Eu NCs is ~6 nm while for β-NaYF<sub>4</sub>:Tb (Fig. 2(c) and (d)) and β-NaYF<sub>4</sub>:Tb,Eu (Fig. 2(e) and (f)) NCs it is close to 4 nm. The values obtained and their trend are similar to our conclusions from p-XRD studies.

Fig. 2(a) shows the emission spectrum obtained at an excitation wavelength of 360 nm. This wavelength is resonant with the 5D<sub>0</sub>–D<sub>2</sub> transition of Tb<sup>3+</sup> ion. As a consequence, characteristic emission lines related to transitions between the 5D<sub>4</sub> energy level and 7F<sub>J</sub> (J = 0, 1, 2, 3) multiplet are observed at 487, 545, 584, 618 nm, respectively.

Owing to the large J values associated with the pertinent terbium energy levels, terbium emission bands normally consist of a large number of transitions which can rarely be fully resolved. Thus, it is not usually possible to infer much about the local symmetry of the metal ion from an analysis of the fine structure. Moreover, β-NaYF<sub>4</sub> crystallizes in a hexagonal structure in which Eu<sup>3+</sup> (Tb<sup>3+</sup>) occupies one of the three possible sites. Two sites are of C<sub>3v</sub> symmetry, which induces a strong asymmetric splitting of the 5D<sub>J</sub> multiplet due to the axial character of these sites symmetry. Nevertheless, it is also possible that 2h site with C<sub>3</sub> symmetry is occupied by Eu (Tb) ions. For all these reasons, the high resolution PL spectrum obtained for the main emission band (5D<sub>4</sub> → 7F<sub>J</sub>) (rhs Fig. 2(a)) has much wider emission broadening than one observed for Eu ions. Thus, it is difficult to discuss the nature of Tb sites in the NaYF<sub>4</sub> matrix.

Fig. 2(e) shows the emission spectrum recorded for the β-NaYF<sub>4</sub>:Eu<sup>3+</sup> sample with an excitation of 395 nm which is in resonance with the transition from the 3H<sub>4</sub> energy level to the 5L<sub>6</sub> excited state.
level of the Eu³⁺ ion. Excitation at this wavelength causes the appearance of four characteristic emission bands related to transitions between the ⁵D₀ energy level and the ⁷Fₓ multiplet’s levels of the Eu³⁺ ion at 696, 612, 590 nm for J = 4, 2, 1, respectively. Additionally, an emission band related to ⁵D₁ → ⁷F₂ transition has been observed at 530 nm and other weak emission band at 550 nm which can be related to ⁵D₂ → ⁷F₄ or ⁵D₁ → ⁷F₃ transitions, respectively. In contrast to the Tb ions, Eu proves to be a more useful ion for emission lineshape analysis, owing to the lower J values associated with the observed transitions. Thus, as with Tb ions a high resolution PL spectrum has been recorded and shown on the right side of Fig. 2(c). From this resulting spectrum, it is evident that the main emission band is a superposition of three sharp and one broad emission bands corresponding to Stark levels of the Eu ion placed at sites with C₃ symmetry and part of the ions is placed at the NC surface. More detailed discussion on the origin of fourth broad band can be found in our previous paper.¹³

Fig. 2(b) shows the emission spectra obtained for β-NaYF₄:Tb sample with excitation wavelengths of 395 and 360 nm. As can be seen (Fig. 3(b)), the emission bands typical for both ions (Eu³⁺ and Tb³⁺) can be observed but only when the sample is excited at 285, 295, 317, 360 and 490 nm (black line). These wavelengths correspond to resonant Tb³⁺ ion excitation and will be discussed in more detail in the next section. On the other hand, when the sample is excited at 395, 465 or 530 nm, only the emission bands related to Eu³⁺ ions can be observed (blue line). These wavelengths correspond to resonant excitation of Eu³⁺ ion. The J = 1 band is magnetic dipole-allowed and is little effected by the changes in the co-ordination environment. Whereas J = 2 band is an electric dipole transition and is sensitive to the environment.

Hence within this approach, the ratio of electric-dipole (⁴D₀→⁷F₂) and magnetic-dipole (⁴D₀→⁷F₁) transitions (R₂/₁) intensities can be used as a measure of distortion around the ion. It has been found that this ratio is approximately equal to one and does not change between NaYF₄:Eu and NaYF₄:Tb, Eu samples. Based on this finding, it can be concluded that co-doping with Tb does not have any significant effect on the local environment of Eu ions. On the other hand, the ratio between ⁴D₀→⁷F₂ and ⁴D₁→⁷F₂ transition intensities (R₀/₁) can give information about the efficiency of nonradiative relaxation from ⁴D₁ down to ⁴D₀. For NaYF₄:Eu sample this value is equal to ~5 while for co-doped sample increases to a value ~12. This observation indicates that the nonradiative relaxation from ⁴D₁ down to ⁴D₀ is much more efficient for the co-doped sample, resulting in much better optical quality. Our experiments (not shown here) in which the optical properties of NaYF₄:Eu samples doped with different Eu concentrations (0.5–20%) suggest that in NaYF₄:Eu (5%) efficient cross-relaxation [(⁴D₁ → ⁴D₀) : (⁷F₀ → ⁷F₃)] between Eu ions takes place resulting in weak emission from the ⁴D₁ level. Thus, an increase in the R₀/₁ ratio from 5 to 12 for co-doped sample suggests that the efficiency of cross-relaxation between Eu ions increases probably due to reduction in effective ion–ion distance.

The selective emission spectrum shown in Fig. 2(b), depending on the excitation wavelength, gives the possibility of using such material as a multi-color emitter. Moreover, this effect indicates that when the Eu³⁺ ions are excited resonantly, no emission from Tb³⁺ occurs. This suggests that the energy transfer from Eu³⁺ to Tb³⁺ is not significant, while the energy transfer from Tb³⁺ to Eu³⁺ is a dominant process responsible for Eu³⁺ emission at shorter excitation wavelengths. To demonstrate above effects,
images of investigated samples have been made at different excitation wavelengths in which a 500 nm edge filter has been used to cut off the excitation beam. As can be seen (Fig. 3) for samples where only one ion has been introduced (Tb or Eu) the color of emission for all excitation wavelengths is almost the same (green or reddish). On the other hand, visible difference can be seen for sample co-doped with two ions, when colors of emission change from green to red when the excitation wavelength is varied.

To better understand the interaction between two ions, the excitation spectra have been collected for all emission lines observed in Fig. 4(b). Fig. 4(a)–(c) show the room temperature PL intensity as a function of both excitation and emission wavelengths (colors describe the PL intensity), for all investigated samples. The cross-section through the maps shown in Fig. 5 gives us the excitation profiles for the particular emission band. This has been done with a high spectral resolution for most intense transitions, i.e. at 612 nm (\( \Delta D_0 \to \Delta F_2 \)) for Eu ions and at 545 nm (\( \Delta D_4 \to \Delta F_1 \)) for Tb\(^{3+} \) ions and is shown in Fig. 5(d)–(f).

In the same way, as in Fig. 2, the vertical bars in Fig. 4(d)–(f) correspond to the calculated f–f transition for a free ion approximation. Moreover, spectral ranges expected for typical 4f–5d transitions have been shown as horizontal bars in Fig. 4(d). Due to the fact that the position of 4f–5d transitions strongly differs from ones obtained for free ion and varies strongly from one matrix to another, estimation of their position has been made based on the data collected for many matrices by P. Dor- enbos.\(^{15} \) For Eu ions, these kinds of transitions are not expected as the excitation bands corresponding to 4f–5d transitions in Eu\(^{3+} \) are over the energies considered in our case (i.e. 8.7 eV).\(^{16} \) The internal charge transfer transition for both ions is also expected to appear at much higher energies (~6.7 to 8.4 eV for fluorides).

Based on comparison between the excitation spectra obtained for NaYF\(_4\):Tb and NaYF\(_4\):Eu and calculated positions of f–f and estimated f–d transitions the interpretation of the excitation bands for these two samples has been given (see labels in Fig. 4(d) and (f)).

Fig. 4(e) shows the excitation spectra obtained for NaYF\(_4\):Tb,Eu sample when the detection has been set at 612 or 545 nm. It can be clearly seen that these two spectra overlap with the ones obtained for samples containing Tb\(^{3+} \) and Eu\(^{3+} \) only (see Fig. 5(d) and (f)). The only difference for the excitation spectrum recorded for Eu emission from NaYF\(_4\):Tb,Eu sample as compared to ones from NaYF\(_4\):Eu sample is that the red emission appears also at wavelengths corresponding to resonant Tb excitation. This result confirms the excitation of Eu ions through the Tb ions. In contrast, green emission has not been observed when the sample was excited with characteristic for Eu wavelengths like 395, 465 and 530 nm. This observation is simply due to the fact that these wavelengths are not in resonance with any transitions of Tb ions but excite Eu ions only and the energy transfer from Eu\(^{3+} \) to Tb\(^{3+} \) is not present; thus, no emission from Tb can be observed at these excitation wavelengths.

Nevertheless, for other excitation wavelengths, the energy levels of Eu\(^{3+} \) ions and Tb\(^{3+} \) ions overlap each other, and the excitation energy exchange is still possible in both directions. Especially, strong Eu\(^{3+} \) emission has been observed at excitation wavelengths corresponding to the 4f \( \to \) 5d transition of Tb\(^{3+} \) ions. These results establish that there exists a strong energy transfer from Tb\(^{3+} \) to Eu\(^{3+} \) ions in this kind of matrix. The full picture of possible emission/excitation transitions is shown in Fig. 5 where energy levels have been calculated for free Eu and Tb ions.

To confirm above conclusions and to get better insight into interaction between both ions the emission decay times have been measured at different excitation wavelengths (see ESI). Most of the traces show long and strongly non-single exponential decay profiles and only for some excitation wavelengths it was possible to fit our data with only one or two simple exponential functions. In order to discuss all data in one theoretical framework all emission decay times have been fitted by a stretched exponential function defined as follow:

\[
PL(t) = I_0 \left( \frac{t}{\tau} \right)^{1-\beta} \exp \left[ -\left( \frac{t}{\tau_0} \right)^{\beta} \right]
\]

(1)
In the above equation $\tau_0$ is an effective time constant, $\beta$ is a constant between 0 and 1, and $I_0$ is a constant. It should be also pointed out that this form of equation means that the fraction of excited emitters $n(t)/m(0)$ is assumed to be given by the Kohlrausch equation

$$n(t)/m(0) = \exp\left[\left(\frac{t}{\tau_0}\right)^\beta\right].$$

The PL decay (eqn (1)) is therefore calculated as a negative time derivative of the Kohlrausch function. The least-squares fit of eqn (1) to experimental data brings values of $\tau_0$ and $\beta$. Having these two constants it is also possible to define average decay time constant ($\tau$):

$$\tau_{\text{obs}} = \langle \tau \rangle = \frac{\tau_0}{\beta} \Gamma\left(\frac{1}{\beta}\right)$$

where $\Gamma$ is the mathematical Gamma function. The complexity of the relaxation path, either within single ion or for Eu coupled to Tb described in our approach by $\beta$ is the mathematical values close to zero which means that the relaxation path is a very complex process. The value close to one describes the situation which can be well-fitted by a single exponential function reflecting a simple two level model of the relaxation process.

The fitting parameters as described above are plotted in Fig. 6. In this figure, the vertical bars represent values obtained for $\beta$ parameters corresponding to averaged decay times plotted in Fig. 6 as squares. Depending on the excitation wavelength, the average decay time for Tb emission in NaYF$_4$:Tb sample increases slightly or is even constant with this temporal resolution when the excitation energy decreases.

If the same emission band is measured for Tb ions co-doped with Eu, the average decay time has been reduced by factor two, from $\sim$4 down to 2 ms. This reduction is due to coupling between the Tb and Eu ions which has been shown by the excitation spectra for both ions. This reduction in emission decay is due to the additional nonradiative path in Tb relaxation becoming active and the observed decay time becomes shorter as: $1/\tau_{\text{obs}} = 1/\tau_\text{R} + \sum 1/\tau_{\text{NR}}$, where a new nonradiative relaxation path for Tb ions related to energy transfer to Eu ($1/\tau_{\text{ET}}$) must be included in $\sum 1/\tau_{\text{NR}}$. In the framework used, it is interesting to analyze the values obtained for the $\beta$ parameter. For samples containing only Tb ions, this value for all excitation wavelengths is above 0.9 and approaches close to 1 at excitation wavelengths longer than 360 nm. Hence, there is no complex relaxation for this sample over all excitation energies range. This result also indicates that at first approximation we can assume that at 5% of Tb there are no significant ion–ion interactions. On the other hand, for the co-doped sample, it can be seen that the $\beta$ parameter takes values smaller than 0.8 and for some excitation wavelengths even close to 0.7. This indicates that in this case, the relaxation path cannot be explained by a single exponential process and much more complex kinetic is involved in the relaxation, i.e. efficient energy transfer from Tb to Eu ions. Back energy transfer is less likely to be the case as Eu emissive state ($^5D_0$) is substantially lower in energy than that of Tb ($^5D_4$) and low probability phonon assisted processes should not be involved in this case.

On analyzing the averaged decay times for the Eu emission it can be seen that there is a much more complex relaxation mechanism in this case. Firstly similar to the Tb emission, the averaged decay times decrease on co-doping with the Tb and Eu ions. The reason for this effect is the same as for the Tb ions and relates to the interaction between Eu and Tb ions. Nevertheless, it can be seen that $\tau_{\text{obs}}$ strongly depends on the excitation energy and its behavior shows a nonlinear dependence. This nonlinear dependence looks very similar for both the samples doped only with Eu and the ones co-doped with both ions (Tb, Eu). This observation may mean that this property has its own origin in only the Eu ions. This nonlinear behavior is kept for the sample with lower Eu content (0.5%), which indicates that the origin of this property is also not in Eu–Eu interactions. This behavior can be explained by the two different Eu sites in our samples i.e. surface related and volume related. Observed emission will have different contribution coming from Eu$^{3+}$ ions placed at the NC surface as well inside the core in different ratios depending on the excitation wavelength. The main excitation path in UV for internal ions is through the resonant excitation of Eu$^{3+}$ ions. For surface related Eu$^{3+}$ ions the main excitation path on UV excitation is through the charge transfer state (CTS) related to ligand groups present at the NaYF$_4$ surface (i.e. TOPO groups). This excitation leads to the relaxation of carriers to the $^5D_0$ level and will be very fast as compared to the low probability multiphonon process dominating relaxation of internal ions. As a consequence, detected decay times will be short and comparable with the one obtained for resonant excitation of $^5D_0$ levels. When the ions are excited in the visible range only the excitation path for both sites (volume and surface) is resonant excitation followed by multiphonon relaxation which is a very slow process for the NaYF$_4$ matrix. As a consequence, the measured decay time will be much longer. Finally, when the ions are excited quasi resonantly to $^1D_2$ levels measured decay time is close to one characteristic for $^3D_0$–$^5F_2$ transition and almost equal to one obtained at UV excitation.

This kind of excitation path is not observed for Tb$^{3+}$ ions since the charge transfer state for terbium is at much higher energies than the ones used in our experiments. It can deduced from the above discussion that the relaxation mechanism in co-doped samples is very complex in which both the ions can decay emission in different ways and within different temporal ranges. The last finding can be used as an advantage in obtaining multicolored emitters where the color of emission can be tuned by changing the emission delay time. An example of such an effect is shown in Fig. 7 where the emission spectrum for NaYF$_4$:Tb,Eu sample has been collected 50 $\mu$s after the pulse (orange line) and

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**Fig. 6** Fitting parameters obtained for all investigated samples when emission decay time spectra have been fitted by stretch exponential function.
10 ms after the pulse (red line). Both spectra have been normalized at 612 nm and the excitation wavelength was 285 nm. Inset in Fig. 7 shows the CEI diagram which shows how the observed colors of samples are changing as the delay time is varied.

Conclusion

In conclusion it has been shown that NaYF₄ co-doped by Eu and Tb ions can be characterized by multicolor emission depending on the excitation wavelength and detection delay time. This property is a consequence of complex interaction between Eu and Tb ions. Except the direct excitation of each ion, the excitation energy is transferred from Tb to Eu ion but not in the opposite direction and, moreover, part of the energy migrates between the Eu ions due to cross-relaxation processes. It has also been demonstrated that the averaged emission decay time for Eu ions in such material is strongly nonlinearly dependent on the excitation energy. This nonlinearity is a consequence of the complicated excitation path for Eu³⁺ ions or, more generally, a consequence of surface sites of Eu ions for which the charge transfer from oxygen atoms takes place at higher excitation energies. On the other hand, existence of such a state may be also accountable for efficient nonradiative relaxation between excited and ground energy levels of europium, strongly reducing the external emission quantum efficiency. In consequence, core–shell structures may be prepared for NaYF₄ matrices doped with Eu³⁺ ions to simplify the excitation/relaxation paths and to increase red emission intensity.

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Notes and references