



# Effect of $\text{Eu}^{3+}$ codoping on upconversion luminescence in $\text{Y}_2\text{O}_3:\text{Er}^{3+}, \text{Yb}^{3+}$ nanocrystals

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## ABSTRACT

The influence of  $\text{Eu}^{3+}$  on the upconversion (UC) fluorescence of  $\text{Er}^{3+}$  in  $\text{Y}_2\text{O}_3:\text{Er}^{3+}, \text{Yb}^{3+}$  nanocrystals was investigated. Room-temperature UC spectra show that the intensity ratio of red to green lights was increased from 8.6 to 19.3 with 1.0 mol%  $\text{Eu}^{3+}$  doping. Additionally, with the increase of  $\text{Eu}^{3+}$  ion concentration, the  $n$  values for both green and red UC emissions in  $\text{Y}_2\text{O}_3:\text{Er}^{3+}, \text{Yb}^{3+}$  nanocrystals become larger. Our analysis shows that the energy transfer between  $\text{Eu}^{3+}$  and  $\text{Er}^{3+}$  ions is the main cause for the enhancement of  $^2\text{H}_{11/2}, ^4\text{S}_{3/2} \rightarrow ^4\text{F}_{9/2}$  and  $^4\text{I}_{11/2} \rightarrow ^4\text{I}_{13/2}$  transitions of  $\text{Er}^{3+}$  ions.

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## 1. Introduction

Recently, rare-earth (RE) doped upconversion (UC) nanocrystals, which have sharp luminescence in the visible range under near-infrared excitation, have attracted a lot of attention for their potential applications in many fields [1–4]. Among the candidates of RE ions, trivalent erbium ( $\text{Er}^{3+}$ ) has excellent UC properties. In the NIR region,  $\text{Er}^{3+}$  has a favorable energy-level structure with two transitions  $^4\text{I}_{15/2} \rightarrow ^4\text{I}_{11/2}$  at 978 nm and  $^4\text{I}_{15/2} \rightarrow ^4\text{I}_{9/2}$  at 800 nm that can be excited with semiconductor lasers, yielding blue, green, and red emissions in the visible range [5–9]. UC luminescence of  $\text{Y}_2\text{O}_3$  nanocrystals codoped with  $\text{Er}^{3+}$  and  $\text{Yb}^{3+}$  ions has been widely investigated. Codoping of  $\text{Yb}^{3+}$  has proven to be a successful alternative for the direct upconversion process.  $\text{Yb}^{3+}$  has a much larger absorption cross section than  $\text{Er}^{3+}$  at 978 nm and can transfer the absorbed energy efficiently to  $\text{Er}^{3+}$  ions, consequently, it can markedly improve the UC efficiency of  $\text{Er}^{3+}$  ions [10]. In addition, yttria is an efficient media for generating UC luminescence, which has a low phonon energy that could increase the radiative transitions, resulting in a higher quantum yield. Moreover, yttria exhibits high chemical durability and thermal stability, which are useful in many practical applications [11].

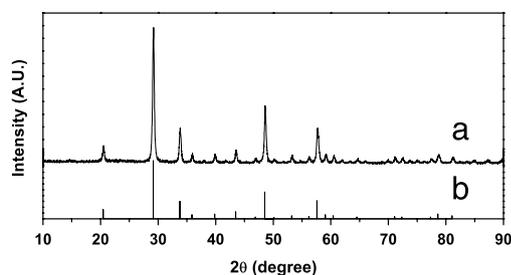
In an earlier work, single green and single red UC radiations in the visible range were produced under 980 nm diode laser excitation in  $\text{ZrO}_2:\text{Er}^{3+}$  and  $\text{ZrO}_2:\text{Er}^{3+}, \text{Yb}^{3+}$  nanocrystals [12], which may be used in multiple color biolabels. In addition,  $\text{Eu}^{3+}$  ions have been codoped into  $\text{Y}_2\text{O}_3:\text{Ho}^{3+}, \text{Yb}^{3+}$  nanocrystals to design a better monochromatic UC green spectrum. In this work, we report an investigation on the resonance energy transfer between  $\text{Er}^{3+}$  and  $\text{Eu}^{3+}$  ions in  $\text{Y}_2\text{O}_3:\text{Er}^{3+}, \text{Yb}^{3+}, \text{Eu}^{3+}$  nanocrystals, which can help understand the effect of  $\text{Eu}^{3+}$  codoping on the UC properties of  $\text{Er}^{3+}$ . Our results show that the energy transfer affects the population of the red and green energy levels, and consequently, improves the monochromaticity of the UC red emission, which is needed in multiple color biolabeling applications.

## 2. Experiment

Nanocrystals  $\text{Y}_2\text{O}_3:1\text{Er}^{3+}, 10\text{Yb}^{3+}$  codoped with different concentrations of  $\text{Eu}^{3+}$  ions were prepared using a complex precursor synthesis procedure. Briefly,  $\text{Y}_2\text{O}_3$  (99.99%),  $\text{Er}_2\text{O}_3$  (99.99%),  $\text{Yb}_2\text{O}_3$  (99.99%) and  $\text{Eu}_2\text{O}_3$  (99.99%) with a corresponding molar ratio of cations were completely dissolved into dilute nitric acid to produce their nitrates. Then, a certain amount of citric acid was added to the nitrate solution. The molar ratio of citric acid to cations was maintained at 4:1 for all samples. Ammonium hydroxide was used to adjust the pH values at 6.0 for all samples. The well-stirred solution was treated at 180 °C for 12 h until it was transformed into charcoal-like porous foam. It was successively milled and heated

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**Fig. 1.** (a) XRD pattern of Y<sub>2</sub>O<sub>3</sub>:Yb<sup>3+</sup>, Er<sup>3+</sup> UC nanocrystals; (b) XRD pattern of pure cubic Y<sub>2</sub>O<sub>3</sub> nanocrystals in JCPDS card.

in a high-temperature oven at 800 °C for 2 h in air to obtain white color powders.

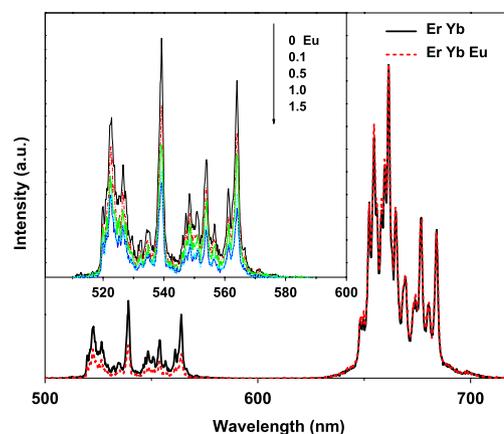
The UC spectra of the powders were excited by a continuous wave 976 nm diode laser and obtained using a lens-coupled monochromator (Zolix SBP 300) with a photomultiplier (Zolix CR131) tube attached. The spectral resolution of the monochromator is about 1 nm.

### 3. Results and discussions

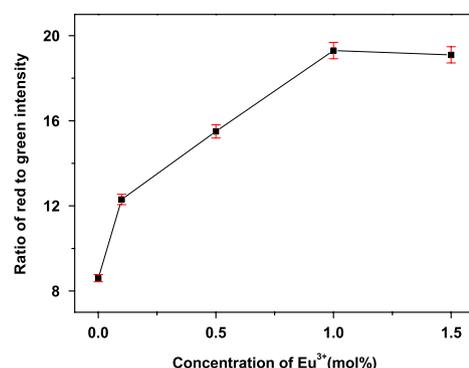
Fig. 1(a) shows the XRD pattern of Y<sub>2</sub>O<sub>3</sub>:Er<sup>3+</sup>, Yb<sup>3+</sup> UC nanocrystals measured by a Rigaku D/max-γB diffractometer. As shown in the figure, the diffraction peaks match well to the standard powder diffraction pattern of cubic Y<sub>2</sub>O<sub>3</sub> (JCPDS 25-1200) (see Fig. 1(b)).

The UC spectra of Y<sub>2</sub>O<sub>3</sub>:1Er, 10Yb nanocrystals codoped with Eu<sup>3+</sup> ions at different concentrations were measured under the excitation of 976 nm NIR diode laser. The observed emission spectra are composed of two distinct emission bands centered around 564 nm and 661 nm, which correspond to <sup>2</sup>H<sub>11/2</sub>, <sup>4</sup>S<sub>3/2</sub> → <sup>4</sup>I<sub>15/2</sub> and <sup>4</sup>F<sub>9/2</sub> → <sup>4</sup>I<sub>15/2</sub> transitions of Er<sup>3+</sup>, respectively. Although the positions of the UC emission peaks have no change with the addition of Eu<sup>3+</sup> ions, the intensities of UC emissions are decreased. Fig. 2 shows the UC fluorescence spectra of Y<sub>2</sub>O<sub>3</sub>:1Er<sup>3+</sup>, 10Yb<sup>3+</sup> and Y<sub>2</sub>O<sub>3</sub>:1Er<sup>3+</sup>, 10Yb<sup>3+</sup>, 1Eu<sup>3+</sup> nanocrystals using the normalized UC red emission bands as the reference. It can be seen that with the addition of Eu<sup>3+</sup> ions, the intensity of green emissions is decreased relative to the intensity of the red emissions. The inset of Fig. 2 shows the green UC emissions in Y<sub>2</sub>O<sub>3</sub>:1Er, 10Yb nanocrystals as a function of Eu<sup>3+</sup> ion concentration using normalized UC red emission bands as the reference. The ratio of integrated intensities of red over green UC radiations has been measured and plotted in Fig. 3; this ratio increases monotonically from 8.6 to 19.3 as the Eu<sup>3+</sup> ion concentration increases from 0 to 1.0 mol%, but when the Eu<sup>3+</sup> ion concentration is beyond 1.0 mol%, the ratio starts to decrease. The monochromaticity of UC emissions can be quantified by the SR parameter [12] defined as  $SR = I_{\text{main}} / (I_{\text{det}} - I_{\text{main}})$ , where  $I_{\text{main}}$  is the integrated intensity of the main band, and  $I_{\text{det}}$  is the overall intensity over the spectral sensitivity range of the optical detector. As shown in Fig. 2,  $I_{\text{main}}$  and  $I_{\text{det}} - I_{\text{main}}$  can be calculated from the green band integrated from 510 to 600 nm and the red band integrated from 600 to 720 nm, respectively. For our case, the SR parameter is equal to the ratio of the integrated intensities of red over green emissions. The obtained SR values indicate that codoping of Eu<sup>3+</sup> ions in the Y<sub>2</sub>O<sub>3</sub>:Er<sup>3+</sup>, Yb<sup>3+</sup> nanocrystals results in the improvement of monochromaticity of the Er<sup>3+</sup> UC red emission.

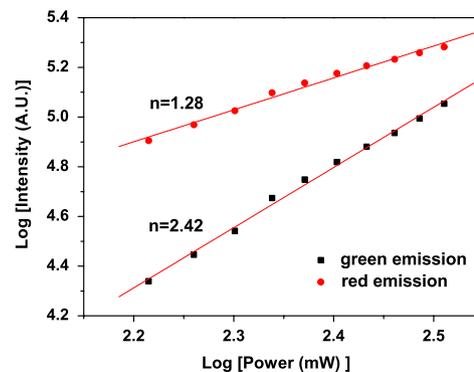
The UC intensity ( $I_{\text{up}}$ ) is proportional to the  $n$ th power of the pumping intensity ( $I_{\text{pump}}$ ), i.e.,  $I_{\text{up}} \propto (I_{\text{pump}})^n$ , where  $n$  is the number of pumping photons required to excite rare-earth ions from the ground state to the emitting state. Fig. 4 shows the log–log plot of UC emission intensity of Y<sub>2</sub>O<sub>3</sub>:1Er, 10Yb nanocrystals as



**Fig. 2.** (Color online) Measured UC spectra of Y<sub>2</sub>O<sub>3</sub>:10 mol% Yb<sup>3+</sup>, 1 mol% Er<sup>3+</sup>. Inset: green emission as a function of Eu<sup>3+</sup> ion concentration normalized with respect to the UC red emission bands.



**Fig. 3.** Green to red emission intensity ratio of Y<sub>2</sub>O<sub>3</sub>:Yb<sup>3+</sup>, Er<sup>3+</sup> UC nanocrystals as a function of Eu<sup>3+</sup> concentrations.



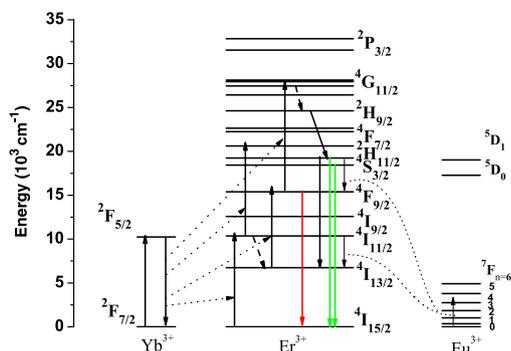
**Fig. 4.** (Color online) Pump power dependence of the green and red upconversion luminescences in Y<sub>2</sub>O<sub>3</sub> nanocrystals doped with 1 mol% Er<sup>3+</sup>, and 10 mol% Yb<sup>3+</sup> ions.

a function of the pump power. The  $n$  values can be determined from the slopes of the curves. We found that  $n$  values of the green (<sup>2</sup>H<sub>11/2</sub>, <sup>4</sup>S<sub>3/2</sub>) → <sup>4</sup>I<sub>15/2</sub> and red <sup>4</sup>F<sub>9/2</sub> → <sup>4</sup>I<sub>15/2</sub> transitions are 2.42 and 1.28, respectively, which deviate significantly from the two-photon processes, which indicate that there are three- and one-photon processes involved in addition to the two photon UC process.

The UC mechanism of rare-earth ions mainly consists of the following processes: excited state absorption, successive energy transfer, cross relaxation, cooperative UC and photon avalanche. Fig. 5 shows the energy level diagram of the Er<sup>3+</sup> and Yb<sup>3+</sup> ions and possible mechanism of UC luminescence. Under a 976 nm laser excitation, the <sup>2</sup>F<sub>5/2</sub> excited state of Yb<sup>3+</sup> has much larger

**Table 1**  
*n* values of green UC emissions.

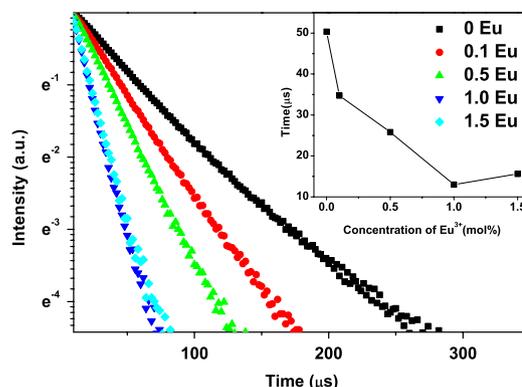
The concentration of Eu <sup>3+</sup> (mol%)	0	0.1	0.5	1.0	1.5
Green emission	2.42 ± 0.04	2.62 ± 0.03	2.79 ± 0.05	3.02 ± 0.06	3.01 ± 0.05



**Fig. 5.** (Color online) Energy level diagrams of Yb<sup>3+</sup>, Er<sup>3+</sup> and Eu<sup>3+</sup> ions and the proposed mechanisms for the generation of UC spectra.

absorption cross section compared to the <sup>4</sup>I<sub>11/2</sub> excited state of Er<sup>3+</sup> so that the energy transfer from Yb<sup>3+</sup> to Er<sup>3+</sup> is the dominant UC mechanism in codoped samples with higher concentrations of Yb<sup>3+</sup>. Under the irradiation by a 976 nm diode laser, the Yb<sup>3+</sup> ion is excited to the <sup>2</sup>F<sub>5/2</sub> state and then transfers its energy to an Er<sup>3+</sup> ion in the ground state, thereby exciting the latter to the <sup>4</sup>I<sub>11/2</sub> intermediate state. The <sup>4</sup>F<sub>7/2</sub> state is populated by another energy transfer process through Yb<sup>3+</sup>. Subsequently, the Er<sup>3+</sup> ions at <sup>4</sup>F<sub>7/2</sub> state are relaxed rapidly to the <sup>2</sup>H<sub>11/2</sub>/<sup>4</sup>S<sub>3/2</sub> state by multi-phonon processes. At higher Yb<sup>3+</sup> ions concentration as in this work, the energy back transfer process <sup>4</sup>S<sub>3/2</sub>(Er<sup>3+</sup>) + <sup>2</sup>F<sub>7/2</sub>(Yb<sup>3+</sup>) → <sup>4</sup>I<sub>13/2</sub>(Er<sup>3+</sup>) + <sup>2</sup>F<sub>5/2</sub>(Yb<sup>3+</sup>) is the main depopulation mechanism of the <sup>4</sup>S<sub>3/2</sub> state, which results in the saturation of the <sup>4</sup>I<sub>13/2</sub> state (Er<sup>3+</sup>) [12]. The <sup>4</sup>F<sub>9/2</sub> state can be populated though energy transfers from an Yb<sup>3+</sup> ion. Therefore, the one-photon process is needed to produce the red UC emission, which is consistent with the measured *n* values. As shown in Fig. 4, the slope of the green UC curve is 2.42, which indicates the participation of a three-photon conversion process in addition to the two-photon process already described above for green UC fluorescence. The three-photon process of green UC emission was also observed in several earlier investigations [13,14]. Some of the ions in the <sup>4</sup>F<sub>9/2</sub> and <sup>4</sup>I<sub>9/2</sub> levels are excited to the <sup>2</sup>H<sub>9/2</sub> and <sup>4</sup>F<sub>5/2</sub> levels via energy transfer through Yb<sup>3+</sup> ions. These ions then return to the <sup>4</sup>G<sub>11/2</sub> and <sup>4</sup>S<sub>3/2</sub> levels by cross-relaxation and nonradiative decays.

As shown in Fig. 5 the energy-levels of Eu<sup>3+</sup> ions have some interesting characteristics, including <sup>7</sup>F<sub>*j*</sub> ladder levels. The spacing within the <sup>7</sup>F<sub>*j*</sub> multiplet of Eu<sup>3+</sup> can be bridged by two or less phonons in Y<sub>2</sub>O<sub>3</sub> host [15–18]. Once the <sup>7</sup>F<sub>*j*</sub> multiplet is populated, the electrons will be depleted to the ground state by non-radiative decays. The energy differences between <sup>4</sup>I<sub>11/2</sub> and <sup>4</sup>I<sub>13/2</sub>, <sup>2</sup>H<sub>11/2</sub> and <sup>4</sup>F<sub>9/2</sub>, <sup>4</sup>S<sub>3/2</sub> and <sup>4</sup>F<sub>9/2</sub> levels of Er<sup>3+</sup> are about 3600 cm<sup>-1</sup>, 3200 cm<sup>-1</sup> and 3000 cm<sup>-1</sup>, respectively, while between the <sup>7</sup>F<sub>4</sub> and <sup>7</sup>F<sub>0</sub> states of Eu<sup>3+</sup> the energy difference is also about 3000 cm<sup>-1</sup>. This well matching of the resonant energy makes the energy transfer between Er<sup>3+</sup> and Eu<sup>3+</sup> easy to occur [15,17]. Therefore, with Eu<sup>3+</sup> codoping in the Y<sub>2</sub>O<sub>3</sub>:1Er, 10Yb nanocrystals, energy transfer between Er<sup>3+</sup> and Eu<sup>3+</sup> ions constitutes an important contribution. By the non-radiation transitions <sup>4</sup>I<sub>11/2</sub> → <sup>4</sup>I<sub>13/2</sub>, <sup>2</sup>H<sub>11/2</sub>, and <sup>4</sup>S<sub>3/2</sub> → <sup>4</sup>F<sub>9/2</sub>, Er<sup>3+</sup> ions transfer energy to a nearby Eu<sup>3+</sup> ion to populate the <sup>7</sup>F<sub>4</sub> excited level, which induce the electrons of <sup>4</sup>I<sub>11/2</sub>, <sup>2</sup>H<sub>11/2</sub> and <sup>4</sup>S<sub>3/2</sub> states. That is to say, the



**Fig. 6.** (Color online) The decay profiles of the <sup>4</sup>S<sub>3/2</sub> → <sup>4</sup>I<sub>15/2</sub> transition in Y<sub>2</sub>O<sub>3</sub> nanocrystals doped with 1 mol% Er<sup>3+</sup>, 10 mol% Yb<sup>3+</sup> and 0–1.5 mol% Eu<sup>3+</sup> ions. Insert: the life time of <sup>4</sup>S<sub>3/2</sub> state as a function of Eu<sup>3+</sup> ion concentration.

energy transfer process responsible for that the population of the <sup>2</sup>H<sub>11/2</sub>, <sup>4</sup>S<sub>3/2</sub> state from the <sup>4</sup>I<sub>11/2</sub> state is greatly hindered by doping Eu<sup>3+</sup> ions. Therefore, the three-photon process of green UC emission is supposed to dominate over the two-photon process, and the green UC radiation is weakened. On the other hand, the electrons population in the <sup>4</sup>I<sub>11/2</sub>, <sup>2</sup>H<sub>11/2</sub> and <sup>4</sup>S<sub>3/2</sub> states are further depleted by non-radiation decay to lower excited states, which is favorable for red UC emission according to the forward analysis. Thus, it is easy to conclude that the codoping of Eu<sup>3+</sup> will greatly increase the intensity ratio of red to green emissions.

In order to show the effect of the codoping, the *n* values of the green UC emissions as a function of the Eu<sup>3+</sup> ion concentration were measured and listed in Table 1. With the increase of Eu<sup>3+</sup> ion content, the *n* values of the green UC emissions from Y<sub>2</sub>O<sub>3</sub>:Er<sup>3+</sup>, Yb<sup>3+</sup> nanocrystals increase from 2.42 to 3.02. These results indicate that green UC emission gradually become a completely three-photon UC process with the adding of Eu<sup>3+</sup> ions. In other words, the population of green emission is contributed by the non-radiative decay from the <sup>4</sup>G<sub>11/2</sub> level. It is reasonable to believe that, the more Eu<sup>3+</sup> ions added, the stronger the energy transfer from Er<sup>3+</sup> ions to Eu<sup>3+</sup> ions would become. So the linear decay would become the dominant depletion mechanism of the <sup>4</sup>I<sub>11/2</sub> level, while UC to the <sup>2</sup>H<sub>11/2</sub> and <sup>4</sup>S<sub>3/2</sub> states can be neglected. In addition, the population of the <sup>4</sup>I<sub>13/2</sub> state will increase the intensity of the red UC emission relative to the green UC emissions. According to the above analysis, the ratio of integrated intensities of red over green UC radiations increases with Eu<sup>3+</sup> ions doped, which can well illustrate the results obtained before.

Fig. 6 displays the decay profiles of the <sup>4</sup>S<sub>3/2</sub> → <sup>4</sup>I<sub>15/2</sub> transition in Y<sub>2</sub>O<sub>3</sub> nanocrystals doped with 1 mol% Er<sup>3+</sup>, 10 mol% Yb<sup>3+</sup> and 0–1.5 mol% Eu<sup>3+</sup> ions. The lifetime of the <sup>4</sup>S<sub>3/2</sub> states was measured to be 50(3) μs for 0 mol% Eu<sup>3+</sup> ions. As the increase of the Eu<sup>3+</sup> ions, the life time of the <sup>4</sup>S<sub>3/2</sub> state decreased. When the concentration of the Eu<sup>3+</sup> ions was about 1.0 mol%, the minimum lifetime, 13(3) μs, is obtained. For Eu<sup>3+</sup> ions higher than 1.0 mol%, there were slight changes of the lifetime. These data indicate that the Er<sup>3+</sup> ions at the <sup>4</sup>S<sub>3/2</sub> state can quickly nonradiatively relax to the <sup>4</sup>F<sub>9/2</sub> state due to the energy transfer between Er<sup>3+</sup> and Eu<sup>3+</sup> ions. Therefore, the decay from <sup>4</sup>S<sub>3/2</sub> to <sup>4</sup>F<sub>9/2</sub> is greatly enhanced as Eu<sup>3+</sup> ions increase, which lead to the better monochromaticity of the Er<sup>3+</sup> UC red emissions. Such conclusion agrees well with the experimental observation in Figs. 2 and 3.

#### 4. Conclusion

In this paper, the effect of  $\text{Eu}^{3+}$  codoping on upconversion luminescence of  $\text{Y}_2\text{O}_3:\text{Er}^{3+}, \text{Yb}^{3+}$  was studied. Based on the energy level characteristics of  $\text{Er}^{3+}$  and  $\text{Eu}^{3+}$ , the nonresonant energy transfer from  $\text{Er}^{3+}$  to  $\text{Eu}^{3+}$  may contribute to the  ${}^2\text{H}_{11/2}, {}^4\text{S}_{3/2} \rightarrow {}^4\text{F}_{9/2}$  and  ${}^4\text{I}_{11/2} \rightarrow {}^4\text{I}_{13/2}$  transitions, resulting in the increase of the intensity ratio of red to green emissions. Additionally, the energy transfer between the states of  $\text{Eu}^{3+}$  and  $\text{Er}^{3+}$  ions changes the population mechanism of  ${}^2\text{H}_{11/2}, {}^4\text{S}_{3/2}$  and  ${}^4\text{F}_{9/2}$  energy levels, causing the increase of the  $n$  values of green UC emissions and decrease of the lifetimes of the  ${}^4\text{S}_{3/2}$  state.

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