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# Enhancement of Eu<sup>3+</sup> Red Upconversion in Lu<sub>2</sub>O<sub>3</sub>: Yb<sup>3+</sup>/Eu<sup>3+</sup> Powders under the Assistance of Bridging Function Originated from Ho<sup>3+</sup> Tridoping

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**S** Supporting Information

**ABSTRACT:** The red upconversion (UC) emission of Eu<sup>3+</sup> ions in Lu<sub>2</sub>O<sub>3</sub>: Yb<sup>3+</sup>/ Eu<sup>3+</sup> powders was successfully enhanced by tridoping Ho<sup>3+</sup> ions in the matrix, which is due to the bridging function of Ho<sup>3+</sup> ions. The experiment data manifest that, in Yb<sup>3+</sup>/Eu<sup>3+</sup>/Ho<sup>3+</sup> tridoped system, the Ho<sup>3+</sup> ions are first populated to the green emitting level  ${}^{5}F_{4}/{}^{5}S_{2}$  through the energy transfer (ET) processes from the excited Yb<sup>3+</sup> ions. Subsequently, the Ho<sup>3+</sup> ions at  ${}^{5}F_{4}/{}^{5}S_{2}$  level can transfer their energy to the Eu<sup>3+</sup> ions at the ground state, resulting in the population of Eu<sup>3+</sup>  ${}^{5}D_{0}$ level. With the assistance of the bridging function of Ho<sup>3+</sup> ion, this ET process is more efficient than the cooperative sensitization process between Yb<sup>3+</sup> ion and Eu<sup>3+</sup> ion. Compared with Lu<sub>2</sub>O<sub>3</sub>: 5 mol % Yb<sup>3+</sup>/1 mol % Eu<sup>3+</sup>, the UC intensity of Eu<sup>3+</sup>  ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$  transition in Lu<sub>2</sub>O<sub>3</sub>: 5 mol % Yb<sup>3+</sup>/1 mol % Eu<sup>3+</sup>/0.5 mol % Ho<sup>3+</sup> is increased by a factor of 8.



# INTRODUCTION

Trivalent rare-earth ion-doped UC luminescent materials can convert light from near-infrared (NIR) region to visible region.<sup>1</sup> Moreover, the UC materials possess a lot of excellent performances, such as low toxicity, negligible autofluorescence background, high photostability, long luminescence lifetime, and sharp emission bandwidths.<sup>2–6</sup> The above intrinsic advantages render the UC materials excellent systems for applications in many areas, such as photodynamic therapy, biomedical imaging, three-dimensional display, and so on.<sup>7–10</sup>

Generally speaking, Yb<sup>3+</sup> ion, which owns a large absorption cross-section of ~980 nm, is the preferred sensitizer for UC luminescence.<sup>11–13</sup> Correspondingly, the rare-earth ions that own appropriate metastable energy levels that match well with the excited level of Yb<sup>3+</sup> ion are usually chosen as the activators, such as  $Er^{3+}$  ion, Ho<sup>3+</sup> ion, and Tm<sup>3+</sup> ion.<sup>14–17</sup> Therefore, the Yb<sup>3+</sup> ion can easily transfer its energy to  $Er^{3+}$  ion, Ho<sup>3+</sup> ion, or Tm<sup>3+</sup> ion through a series of energy transfer (ET) processes, and then UC luminescence can eventually be realized. However, some certain rare-earth ions without the suitable metastable energy level, such as  $Eu^{3+}$  ion and Tb<sup>3+</sup> ion, can also produce UC luminescence with Yb<sup>3+</sup> ion as the sensitizer through a cooperative sensitization process.<sup>18–21</sup> More specifically, utilizing a cooperative sensitization process, a pair of sensitizers  $Yb^{3+}$  ions can transfer their energy to one nearby activator ion in the ground state simultaneously without the assistance of intermediate energy level.<sup>22,23</sup> In this way, the activator ion can be populated at the high energy state, resulting in the UC emission.

Nevertheless, the emission intensity of the UC luminescence that occurred due to the cooperative sensitization process is much weaker than that by the ET process because of the large energy-level gap between sensitizers and activators. Recently, several groups have reported the improvement of the cooperative sensitization UC process.<sup>24,25</sup> For instance, Yan et al. have realized the UC enhancement of Yb<sup>3+</sup>/Tb<sup>3+</sup> and Yb<sup>3+</sup>/Eu<sup>3+</sup> in NaGdF<sub>4</sub> nanoparticles through building a core– shell structure, and Qiu et al. have achieved the increased UC intensity of Yb<sup>3+</sup>/Tb<sup>3+</sup> in NaYF<sub>4</sub> by tridoping optically inert ions Li<sup>+</sup>.<sup>26,27</sup> However, as far as we know, there is hardly any investigation concerning the cooperative sensitization of UC enhancement realized by changing the ET processes from doping rare-earth luminescent centers.

In current research, the UC properties of  $Yb^{3+}$  and  $Eu^{3+}$  codoped  $Lu_2O_3$  have been carefully explored by the visible and

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NIR spectra as well as the decay curves. The experiment data show that, although the ET process from Yb<sup>3+</sup> ions to Eu<sup>3+</sup> ions can occur through a cooperative sensitization process, the UC intensity of Eu<sup>3+</sup> ions is very weak. Therefore, the Ho<sup>3+</sup> ions are employed as the bridging ions between Yb<sup>3+</sup> ions and Eu<sup>3+</sup> ions for the aim of increasing the Eu<sup>3+</sup> UC intensity. Fortunately, compared with the Yb<sup>3+</sup>/Eu<sup>3+</sup> codoped Lu<sub>2</sub>O<sub>3</sub> powders, the Eu<sup>3+</sup> UC intensities of the Yb<sup>3+</sup>/Eu<sup>3+</sup>/Ho<sup>3+</sup> tridoped samples are sharply enhanced, resulting from the bridging function of Ho<sup>3+</sup> ions. In addition, the ET mechanisms in Yb<sup>3+</sup>/Eu<sup>3+</sup>/Ho<sup>3+</sup> tridoped Lu<sub>2</sub>O<sub>3</sub> are also illuminated in detail.

### EXPERIMENTAL SECTION

**Chemicals.** SpecPure grade rare-earth oxides  $(Eu_2O_3, Ho_2O_3, Yb_2O_3, Lu_2O_3, 99.99\%)$ , obtained from Beijing Founde Star Science and Technology Company Limited, were employed as starting materials without further purification.

Synthesis of Lu<sub>2</sub>O<sub>3</sub>: 5 mol % Yb<sup>3+</sup>/x mol % Eu<sup>3+</sup>/y mol % Ho<sup>3+</sup>. The Lu<sub>2</sub>O<sub>3</sub>: 5 mol % Yb<sup>3+</sup>/x mol % Eu<sup>3+</sup>/y mol % Ho<sup>3+</sup> powders were prepared by the conventional high-temperature solid-state method, specifically as follows. Weigh the starting materials proportionally, add them in an agate mortar, mix them homogeneously for 30 min, move the powders to an alumina crucible with a lid, and then sinter in a box furnace at 1550 °C for 5 h in air.

**Characterization.** Powder X-ray diffraction (XRD) data were identified by Cu K $\alpha$  radiation ( $\lambda = 1.54056$  Å) on a Bruker D8 advance diffractometer. An FLS920 spectrometer purchased from Edinburgh Instruments was used to collect the visible and NIR spectral data. The fluorescence lifetimes were recorded by a Tektronix digital oscilloscope (TDS 3052) equipped with an optical parametric oscillator (OPO) as the excitation source. The lifetimes were calculated by integrating the area under the corresponding lifetime curves with the normalized initial intensity.

#### RESULTS AND DISCUSSION

**Structure.** The XRD patterns for  $Lu_2O_3$ : 5 mol %  $Yb^{3+}/x$  mol %  $Eu^{3+}/y$  mol %  $Ho^{3+}$  powders are collected and depicted in Figure 1. The positions and relative intensity of the



**Figure 1.** XRD patterns of  $Lu_2O_3$ : 5 mol % Yb<sup>3+</sup>/x mol % Eu<sup>3+</sup>/y mol % Ho<sup>3+</sup> powders with the standard XRD data of cubic  $Lu_2O_3$  (JCPDS No. 43–1021).

diffraction peaks for each sample exhibit a single cubic phase  $Lu_2O_3$  with space group *Ia3* (No. 206), corresponding to the standard Card No. JCPDS 43–1021, declaring that the Yb<sup>3+</sup> ions, Eu<sup>3+</sup> ions, and Ho<sup>3+</sup> ions are all incorporated into  $Lu_2O_3$  matrix to form a so-called "solid solution structure".

The UC Properties of Lu<sub>2</sub>O<sub>3</sub>: Yb<sup>3+</sup>/Eu<sup>3+</sup> Powders. Figure 2 shows the emission spectra of Lu<sub>2</sub>O<sub>3</sub>: Yb<sup>3+</sup>/Eu<sup>3+</sup> powders with a fixed concentration of Yb<sup>3+</sup> 5 mol % and various Eu<sup>3+</sup> concentrations under 980 nm wavelength excitation. For the  $Eu^{3+}$ -free sample, there is no emission peak existing in the range of 580-630 nm. However, for the Yb3+ ions and Eu3+ ions codoped samples, three typical Eu<sup>3+</sup> ions emission bands can be monitored distinctly, including the  $Eu^{3+} {}^5D_0 \rightarrow {}^7F_0$  transition that peaked at 586 nm, the Eu<sup>3+</sup>  ${}^{5}D_{0} \rightarrow {}^{7}F_{1}$  transition that peaked at 500 hm, the Eu<sup>3+</sup>  ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$  transition that peaked at 610 nm. Since the Eu<sup>3+</sup> ions cannot be excited directly by 980 nm wavelength, Yb<sup>3+</sup> ions can transfer their energy to Eu<sup>3+</sup> ions, and then the UC phenomenon of Eu<sup>3+</sup> ions can happen.<sup>19</sup> Meanwhile, the UC intensity is enhanced first when the Eu<sup>3+</sup> doping concentration increases from 0 to 1 mol % and then is decreased dramatically resulting from the Eu<sup>3+</sup> concentration quenching. That is to say, the optimum concentration of Eu<sup>3+</sup> ions is 1 mol % in this case.

To offer further evidence for the ET from Yb<sup>3+</sup> ions to Eu<sup>3+</sup> ions, the NIR region spectra of Yb<sup>3+</sup> ions in Lu<sub>2</sub>O<sub>3</sub>: 5 mol %  $Yb^{3+}/x \mod \% Eu^{3+}$  powders excited by 980 nm wavelength are measured and shown in Figure 3a. As described in Figure 3a, two emission bands exist in the range of 1000-1100 nm, peaked at 1030 and 1078 nm, respectively, all belonging to the  ${}^{12}F_{5/2} \rightarrow {}^{2}F_{7/2}$  transition of Yb<sup>3+</sup> ions. Furthermore, when the Eu<sup>3+</sup> ions concentration raises from 0 to 2 mol %, the intensity of  $Yb^{3+2}F_{5/2} \rightarrow {}^2F_{7/2}$  transition is reduced, certifying the existence of ET from Yb<sup>3+</sup> ions to Eu<sup>3+</sup> ions. The decay curves of the as-prepared powders are also collected under 980 nm wavelength excitation. Seen from Figure 3b, it can be noticed that the lifetimes present a falling tendency with the increased Eu<sup>3+</sup> ion doping concentration, demonstrating that the Eu<sup>3+</sup> ion doping provides a new route for Yb<sup>3+</sup> ions to decay: ET from Yb<sup>3+</sup> ions to Eu<sup>3+</sup> ions. Moreover, the decay of Yb<sup>3+</sup> ions is very fast in the beginning period and then becomes slow. This can be explained as follows: in Yb<sup>3+</sup> and Eu<sup>3+</sup> codoped system, under 980 nm wavelength excitation, the population of <sup>5</sup>D<sub>2</sub> level of Eu<sup>3+</sup> ion needs to obtain energy from two nearby excited Yb<sup>3+</sup> ions simultaneously, which will be demonstrated in the following paragraph; in lifetime measurement, after being irradiated by 980 nm pulsed laser, a certain amount of Yb<sup>3+</sup> ions around the  $\mathrm{Eu}^{3+}$  ions are excited to  $^{2}\mathrm{F}_{5/2}$  level; therefore, the ET process from Yb<sup>3+</sup> ions to Eu<sup>3+</sup> ions is very efficient in this period, resulting in the fast decay of Yb<sup>3+</sup> ions; with the expenditure of the excited Yb<sup>3+</sup> ions, the Eu<sup>3+</sup> ions are difficult to receive energy from two nearby excited Yb<sup>3+</sup> ions simultaneously, giving rise to the decrease of the decay rate of Yb<sup>3+</sup> ions. Utilizing the decay curves, the decay times of the synthesized powders can be acquired, and then the ET efficiency  $\eta_{\text{ETE}}$  can be obtained by the following equation

$$\eta_{\text{ETE,Eu}(x\%)} = 1 - \tau_{\text{Eu}(x\%)} / \tau_{\text{Eu}(0)}$$

where  $\tau_{Eu(x\%)}$  is the decay time of  $Yb^{3+}{}^5F_{5/2}$  level with different  $Eu^{3+}$  ion doping concentration, and  $\tau_{Eu(0)}$  represents the decay time of  $Yb^{3+}{}^5F_{5/2}$  level in  $Eu^{3+}$ -free sample. Consequently, the calculated values of the ET efficiency for  $Lu_2O_3$ : 5 mol %  $Yb^{3+}/1$  mol %  $Eu^{3+}$  and  $Lu_2O_3$ : 5 mol %  $Yb^{3+}/2$  mol %  $Eu^{3+}$  are 6.89% and 31.12%, respectively.

According to the previous reports, the UC emission intensity *I* should depend on the pump intensity *P* via the equation  $I \propto P^n$ , where *n* represents the number of the required NIR photons for emitting one visible photon and can be obtained by the



**Figure 2.** Emission spectra of  $Lu_2O_3$ : 5 mol %  $Yb^{3+}/x$  mol %  $Eu^{3+}$  powders (x = 0, 0.1, 0.5, 1.0, 2.0) in the range of 580–630 nm excited by 980 nm wavelength.



**Figure 3.** (a) The NIR spectra of  $Lu_2O_3$ : 5 mol % Yb<sup>3+</sup>/x mol % Eu<sup>3+</sup> powders (x = 0, 0.1, 0.5, 1.0, 2.0) excited by 980 nm wavelength. (b) The decay curves of Yb<sup>3+2</sup>F<sub>5/2</sub> level in  $Lu_2O_3$ : 5 mol % Yb<sup>3+</sup>/x mol % Eu<sup>3+</sup> powders (x = 0, 1.0, 2.0) excited by 980 nm wavelength.

slope of the double logarithmic plots between I and P.<sup>28,29</sup> Hence, to explore the detailed ET mechanism in Yb<sup>3+</sup> and Eu<sup>3+</sup> codoped system, the relationship between the UC intensity of  $Eu^{3+5}D_0 \rightarrow {}^7F_2$  transition in  $Lu_2O_3$ : 5 mol % Yb<sup>3+</sup>/1 mol % Eu<sup>3+</sup> powder and the 980 nm wavelength pump power was investigated. As shown in Figure 4, the *n* value is  $\sim 1.95$ , close to integer 2, manifesting a two-photon process for Eu<sup>3+</sup>  ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$  transition. Therefore, on the basis of the energy-level positions of Yb<sup>3+</sup> ions and Eu<sup>3+</sup> ions, we propose that, in Yb<sup>3+</sup> and Eu<sup>3+</sup> codoped system, under 980 nm wavelength excitation, two excited Yb<sup>3+</sup> ions can transfer their energy to one nearby Eu<sup>3+</sup> ion in the ground state simultaneously by cooperative sensitization process, and then the  $Eu^{3+}$  ion is populated to  ${}^{5}D_{2}$ level. Subsequently, the  $Eu^{3+}$  ion in  ${}^{5}D_{2}$  level can relax nonradiatively to  ${}^{5}D_{0}$  level followed by the red UC emission, as depicted in Figure 5.

The UC Properties of Lu<sub>2</sub>O<sub>3</sub>: Yb<sup>3+</sup>/Eu<sup>3+</sup>/Ho<sup>3+</sup> Powders. On the basis of the above narrative, it can be seen clearly that, although Yb<sup>3+</sup> ions can transfer their energy to Eu<sup>3+</sup> ions, this ET process is not very efficient, resulting in a weak  ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$  transition, due to the large energy level mismatch between Yb<sup>3+</sup>



Figure 4. Power dependence curve of Eu^{3+}  $^5D_0 {\rightarrow}^7F_2$  transition in Lu<sub>2</sub>O<sub>3</sub>: 5 mol % Yb^{3+}/1 mol % Eu^{3+} powder excited by 980 nm wavelength.

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Figure 5. Energy levels of  $Yb^{3+}$  ions and  $Eu^{3+}$  ions along with the involved ET processes.

ions and Eu<sup>3+</sup> ions. To enhance the UC emission of Eu<sup>3+</sup>  ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$  transition, the Lu<sub>2</sub>O<sub>3</sub>: 5 mol % Yb<sup>3+</sup>/1 mol % Eu<sup>3+</sup> powders tridoped with various Ho<sup>3+</sup> ions concentration were prepared, trying to employ Ho<sup>3+</sup> ion as a bridging ion between Yb<sup>3+</sup> ion and Eu<sup>3+</sup> ion to achieve this goal.

Figure 6 describes the UC spectra of Lu<sub>2</sub>O<sub>3</sub>: 5 mol % Yb<sup>3+</sup>/1 mol % Eu<sup>3+</sup>/y mol % Ho<sup>3+</sup> powders as a function of Ho<sup>3+</sup> doping contents. As the Ho<sup>3+</sup> doping content increased from 0 to 2 mol %, the Eu<sup>3+</sup> UC intensity is dramatically enhanced first and then is decreased. The corresponding Ho<sup>3+</sup> doping concentration for the maximum UC intensity of Eu<sup>3+</sup>  $^{5}D_{0}\rightarrow^{7}F_{2}$  transition is 0.5 mol %. Considering both of the Ho<sup>3+</sup> ions and Eu<sup>3+</sup> ions cannot be excited directly by 980 nm wavelength, we propose that the Ho<sup>3+</sup> ions play a role of bridge during the ET process from Yb<sup>3+</sup> ions to Eu<sup>3+</sup> ions, resulting in the Eu<sup>3+</sup> UC enhancement. The related demonstration of the Ho<sup>3+</sup> ion bridging function will be provided in the following paragraphs. Besides, the decrease of Eu<sup>3+</sup> UC intensity as the Ho<sup>3+</sup> doping concentration quenching. Followed by the increase of

 $\text{Ho}^{3+}$  doping concentration from 0 to 2 mol %, the UC emission intensity of  $\text{Ho}^{3+}$  ions (see Figure S1) owns the similar variation trend with that of  $\text{Eu}^{3+}$  ions, suggesting 0.5 mol % is also the optimal concentration for  $\text{Ho}^{3+}$  UC emission in this case. That is to say, when the  $\text{Ho}^{3+}$  doping content is beyond 0.5 mol %, the  $\text{Ho}^{3+}$  concentration quenching phenomenon occurs, which hinders the ET process between  $\text{Ho}^{3+}$  ions and  $\text{Eu}^{3+}$  ions, giving rise to the decrease of  $\text{Eu}^{3+}$  UC intensity.

The Lu<sub>2</sub>O<sub>3</sub>: 5 mol % Yb<sup>3+</sup>/x mol % Eu<sup>3+</sup>/0.5 mol % Ho<sup>3+</sup> powder (x = 0, 0.1, 0.5, 1.0, 2.0) was synthesized to investigate the Ho<sup>3+</sup> ions bridging function between Yb<sup>3+</sup> ions and Eu<sup>3+</sup> ions. As depicted in Figure 7, the UC intensity of Eu<sup>3+</sup> is strongly enhanced and then reduced with the increase of Eu<sup>3+</sup> doping content. The optimal Eu<sup>3+</sup> doping concentration appears at 1 mol % for its UC emission, which is the same as that of Yb<sup>3+</sup> ions and Eu<sup>3+</sup> ions codoped system. Compared with Lu<sub>2</sub>O<sub>3</sub>: 5 mol % Yb<sup>3+</sup>/1 mol % Eu<sup>3+</sup> powder, the UC intensity of Eu<sup>3+ 5</sup>D<sub>0</sub> $\rightarrow$ <sup>7</sup>F<sub>2</sub> transition in Lu<sub>2</sub>O<sub>3</sub>: 5 mol % Yb<sup>3+</sup>/1 mol %  $Eu^{3+}/0.5$  mol %  $Ho^{3+}$  powder is increased by a factor of 8, as exhibited in Figure 8. However, as the increase of Eu<sup>3+</sup> concentration, the UC emission intensity of Ho<sup>3+</sup> is reduced distinctly (see Figure S2), which is a direct proof for the existence of ET from Ho<sup>3+</sup> ions to Eu<sup>3+</sup> ions. Moreover, the decay times of the green emitting level  ${}^{5}F_{4}/{}^{5}S_{2}$  of Ho<sup>3+</sup> are also decreased with the increased Eu<sup>3+</sup> concentration (see Figure 9), providing another evidence for the ET between Ho3+ ions and Eu<sup>3+</sup> ions. Considering the Ho<sup>3+</sup> ion cannot be excited directly by 980 nm wavelength, it can be concluded that the Ho<sup>3+</sup> ions play a role of bridge during the ET process from Yb<sup>3+</sup> ion to Eu<sup>3+</sup> ion. By the utilization of the ET efficiency calculation formula mentioned above, the  $\eta_{\text{ETE}}$  of Ho<sup>3+ 5</sup>F<sub>4</sub>/<sup>5</sup>S<sub>2</sub> level of the samples with different Eu<sup>3+</sup> doping concentrations was acquired and listed in Table 1. Obviously, excited by 980 nm wavelength, the ET from Ho<sup>3+</sup> ions to Eu<sup>3+</sup> in Yb<sup>3+</sup>/Eu<sup>3+</sup>/Ho<sup>3+</sup> tridoped system is more efficient than the ET from Yb<sup>3+</sup> ions to Eu<sup>3+</sup> in  $Yb^{3+}/Eu^{3+}$  codoped system.

The 980 nm wavelength pump power dependence of the UC intensity of  $Eu^{3+} {}^5D_0 \rightarrow {}^7F_2$  transition in  $Lu_2O_3$ : 5 mol % Yb<sup>3+</sup>/1



Figure 6. UC emission spectra of  $Lu_2O_3$ : 5 mol % Yb<sup>3+</sup>/1 mol % Eu<sup>3+</sup>/y mol % Ho<sup>3+</sup> powders (y = 0, 0.1, 0.5, 1.0, 1.5, 2.0) in the range of 580–630 nm excited by 980 nm wavelength.



Figure 7. UC emission spectra of  $Lu_2O_3$ : 5 mol % Yb<sup>3+</sup>/x mol % Eu<sup>3+</sup>/0.5 mol % Ho<sup>3+</sup> powders (x = 0, 0.1, 0.5, 1.0, 2.0) in the range of 580–630 nm excited by 980 nm wavelength.



**Figure 8.** Normalized integral intensity of Eu<sup>3+ 5</sup>D<sub>0</sub> $\rightarrow$ <sup>7</sup>F<sub>2</sub> transition in Lu<sub>2</sub>O<sub>3</sub>: 5 mol % Yb<sup>3+</sup>/x mol % Eu<sup>3+</sup> powders and Lu<sub>2</sub>O<sub>3</sub>: 5 mol % Yb<sup>3+</sup>/x mol % Eu<sup>3+</sup>/0.5 mol % Ho<sup>3+</sup> powders under 980 nm wavelength excitation.



**Figure 9.** Decay curves of  $\text{Ho}^{3+5}\text{F}_4/^5\text{S}_2\rightarrow^5\text{I}_8$  transition in  $\text{Lu}_2\text{O}_3$ : 5 mol %  $\text{Yb}^{3+}/x$  mol %  $\text{Eu}^{3+}/0.5$  mol %  $\text{Ho}^{3+}$  powders (x = 0, 0.1, 0.5, 1.0, 2.0) under 980 nm wavelength excitation.

Table 1. Lifetimes and  $\eta_{\text{ETE}}$  of Ho<sup>3+ 5</sup>F<sub>4</sub>/<sup>5</sup>S<sub>2</sub> Level in Lu<sub>2</sub>O<sub>3</sub>: 5 mol % Yb<sup>3+</sup>/x mol % Eu<sup>3+</sup>/0.5 mol % Ho<sup>3+</sup> Powders (x = 0, 0.1, 0.5, 1.0, 2.0) under 980 nm Wavelength Excitation

concentration of $Eu^{3+}$ (mol %)	lifetime $(\mu s)$	$\eta_{\mathrm{ETE}}$ (%)
0	229.7	0
0.1	188.7	17.85
0.5	172.0	25.12
1.0	130.3	43.27
2.0	63.2	72.49
1.0 2.0	130.3 63.2	43.27 72.49

mol % Eu<sup>3+</sup>/0.5 mol % Ho<sup>3+</sup> powder was measured and shown in Figure 10. The *n* value is 1.91, signifying the Eu<sup>3+</sup>  ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$  transition remains a two-photon process in Yb<sup>3+</sup>/Eu<sup>3+</sup>/Ho<sup>3+</sup> tridoped system. Figure 11 delineates the involved ET processes among Yb<sup>3+</sup> ions, Ho<sup>3+</sup> ions, and Eu<sup>3+</sup> ions. Under 980 nm wavelength excitation, the Yb<sup>3+</sup> ions in the ground state can be excited to  ${}^{2}F_{5/2}$  level by absorbing one 980 nm photon. Next, the excited Yb<sup>3+</sup> ions can transfer their energy to the



**Figure 10.** Power dependence curve of  $Eu^{3+} {}^5D_0 \rightarrow {}^7F_2$  transition in  $Lu_2O_3$ : 5 mol % Yb<sup>3+</sup>/1 mol % Eu<sup>3+</sup>/0.5 mol % Ho<sup>3+</sup> powder excited by 980 nm wavelength.





Ho<sup>3+</sup> ions through the ET1 and ET3 processes, and then the green emitting level  ${}^{5}F_{4}/{}^{5}S_{2}$  of the Ho<sup>3+</sup> ions are populated. The Ho<sup>3+</sup> ions at  ${}^{5}I_{6}$  level can relax nonradiatively to the  ${}^{5}I_{7}$ level and then receive energy from Yb<sup>3+</sup> ions via ET2 process, resulting in the population of the red-emitting level  ${}^{5}F_{5}$  of the Ho<sup>3+</sup> ions. Besides, <sup>5</sup>F<sub>5</sub> level of Ho<sup>3+</sup> ions can also be populated by the nonradiative relaxation process from the  ${}^{5}F_{4}/{}^{5}S_{2}$  level and the cross relaxation (CR) process between  ${}^{5}F_{4}/{}^{5}S_{2}$  level and <sup>5</sup>I<sub>7</sub> level. As for the population of Eu<sup>3+</sup> ions, since the energy levels of Ho<sup>3+</sup> ions match the  ${}^{2}F_{5/2}$  level of Yb<sup>3+</sup> ions much better than that of Eu<sup>3+</sup> ions, it is difficult for Eu<sup>3+</sup> ions to receive energy directly from Yb<sup>3+</sup> ions. Nevertheless, the Eu<sup>3+</sup> ions in the ground state can remain excited by 980 nm wavelength, because of the bridging function of Ho<sup>3+</sup> ions. The Ho<sup>3+</sup> ions at  ${}^{5}F_{4}/{}^{5}S_{2}$  level can transfer their energy to the Eu<sup>3+</sup> ions by ET4 process, resulting in the population of  $Eu^{3+} {}^{5}D_{0}$  level. The radiative transitions from  $Eu^{3+} {}^{5}D_{0}$  level to  ${}^{7}F_{0}$  level,  ${}^{7}F_{1}$  level, and  ${}^{7}F_{2}$  level give rise to the red UC emission, centered at 586, 592, and 610 nm, respectively.

# CONCLUSIONS

In summary, the UC properties of Yb<sup>3+</sup> and Eu<sup>3+</sup> codoped Lu<sub>2</sub>O<sub>3</sub> have been investigated in detail. Under 980 nm wavelength excitation, one Eu<sup>3+</sup> ion can gain energy from two excited Yb<sup>3+</sup> ions simultaneously via a cooperative sensitization process, resulting in the red UC emission. However, because of the large energy-level mismatch between  $Yb^{3+}$  ion and  $Eu^{3+}$  ion, it is inefficient for the  $Eu^{3+}$  UC emission. Therefore, the Ho<sup>3+</sup> ions tridoped Lu<sub>2</sub>O<sub>3</sub>: Yb<sup>3+</sup>/Eu<sup>3+</sup> powders were synthesized for the attempt to change the ET processes between Yb3+ ions and Eu3+ ions and then realize the UC emission improvement of Eu<sup>3+</sup> ions. The experiment data indicate that, in Yb<sup>3+</sup>/Eu<sup>3+</sup>/Ho<sup>3+</sup> tridoped system, the Ho<sup>3+</sup> ions can play a role of bridge between  $Yb^{3+}$  ions and  $Eu^{3+}$  ions. Under 980 nm wavelength excitation, the excited Yb<sup>3+</sup> ions first transfer their energy to Ho<sup>3+</sup> ions, generating the population of  $Ho^{3+} {}^{5}F_{4}/{}^{5}S_{2}$  level. Subsequently, the Eu<sup>3+</sup> ions can be populated to  ${}^5D_0$  level by receiving energy from the Ho<sup>3+</sup> ions at  ${}^{5}F_{4}/{}^{5}S_{2}$  level, which is more efficient than the cooperative sensitization process between  $Yb^{3+}$  ions and  $Eu^{3+}$ ions. With the assistance of the bridging function of  $Ho^{3+}$  ions, the red UC intensity of Eu<sup>3+</sup> ions is increased obviously. Compared with  $Lu_2O_3$ : 5 mol % Yb<sup>3+</sup>/1 mol % Eu<sup>3+</sup>, the UC

intensity of  $Eu^{3+5}D_0 \rightarrow {}^7F_2$  transition in  $Lu_2O_3$ : 5 mol % Yb<sup>3+</sup>/1 mol %  $Eu^{3+}/0.5$  mol % Ho<sup>3+</sup> is increased almost 8 times.

# ASSOCIATED CONTENT

# Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.7b02086.

The UC spectra of  $Lu_2O_3$ : Yb<sup>3+</sup>/Eu<sup>3+</sup>/Ho<sup>3+</sup> powders in the range of 500–700 nm (PDF)

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### Notes

The authors declare no competing financial interest.

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