## Inorganic Chemistry

# Enhanced ${\sim}2~\mu m$ Emission of $Tm^{3+}$ in $Lu_2O_3$ by Addition of a Trace Amount of $Er^{3+}$

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**ABSTRACT:** Er<sup>3+</sup>-induced intensity enhancement of ~2  $\mu$ m emission is observed in 2 atom % Tm<sup>3+</sup> doped Lu<sub>2</sub>O<sub>3</sub> under 782 nm excitation. The maximum enhancement reaches 41.9% with only 0.05 atom % Er<sup>3+</sup>. Er<sup>3+</sup> introduces a new quantum cutting process which is proved to be a Tm<sup>3+</sup>  $\rightarrow$  Er<sup>3+</sup>  $\rightarrow$  Tm<sup>3+</sup> forward–backward energy transfer (FBET) system. The FBET system is observed to work efficiently even at very low Er<sup>3+</sup> concentration. Thus, energy loss due to energy migration among Tm<sup>3+</sup> ions is suggested to be suppressed by the FBET process. The Tm<sup>3+</sup>  $\rightarrow$  Er<sup>3+</sup>  $\rightarrow$  Tm<sup>3+</sup> FBET system may be a new route to improve the performance of Tm<sup>3+</sup> lasers.



## INTRODUCTION

Laser wavelength around the  $\sim 2 \ \mu m$  spectral range has been applied in medical science, laser radar, and remote sensing in the past few years.<sup>1–5</sup> The amazing properties of a  $\sim 2 \ \mu m$  laser include transmission in both atmosphere and common silica fiber, harmless to the eye, and appropriate penetration depth in organization.<sup>6</sup> Thus, researchers have developed different kinds of light sources for  $\sim 2 \ \mu m$  lasers. Tm<sup>3+</sup>-doped Lu<sub>2</sub>O<sub>3</sub> was one of the desired laser media.<sup>7,8</sup> Lu<sub>2</sub>O<sub>3</sub> has higher thermal conductivity (11.3  $Wm^{-1}K^{-1}$ ) in comparison with YAG (6.8  $Wm^{-1}K^{-1}$ ). This is important for heat removal in the pumping process. Emission of Tm<sup>3+</sup> in Lu<sub>2</sub>O<sub>3</sub> has a longer wavelength. This ensures a longer laser wavelength and promises a wider application field of Tm<sup>3+</sup> lasers. The absorption of the Tm<sup>3+</sup> ion in  $Lu_2O_3$  is around 796 nm and matches well with commercially available GaAlAs laser diodes.<sup>9</sup> In the past decades, Lu<sub>2</sub>O<sub>3</sub>:Tm<sup>3+</sup> realized 2.03–2.10  $\mu$ m lasers in forms such as CW lasers, Q-switched lasers, mode-locked lasers, and thin-disk lasers.<sup>10-14</sup> The laser with Lu<sub>2</sub>O<sub>3</sub>:Tm<sup>3+</sup> has been applied as a hybrid booster, in optical parametric oscillation (OPO), as a pump source, etc.<sup>15,10</sup>

When the  ${}^{3}H_{4}$  level of Tm<sup>3+</sup> is excited, the  ${}^{3}F_{4}$  level (~2  $\mu$ m) of Tm<sup>3+</sup> is populated by a cross-relaxation (CR) process.<sup>17,18</sup> This process occurs between two nearby Tm<sup>3+</sup> ions and is essentially a quantum cutting phenomenon. Theoretically, the quantum efficiency is 2 for an ideal CR process. As matter of fact, the efficiency of CR depends on the doping concentration of Tm<sup>3+</sup> ions. With increasing Tm<sup>3+</sup> concentration, both CR efficiency and energy migration between Tm<sup>3+</sup> ions increases.<sup>19,20</sup> If the energy migrates to a Tm<sup>3+</sup> ion with defects around it, the luminescence is quenched. Thus, the best

concentration must be optimized considering the balance between CR efficiency and quenching. In  $Lu_2O_3$ , a 9.3 W laser was achieved with 2 atom % Tm<sup>3+,10</sup> Further increase in CR efficiency is necessary but is also a challenge.

There are limited methods to increase CR efficiency. The common method is introducing ions such as Li<sup>+</sup>, La<sup>3+</sup>, etc. for charge (radius) compensation or better crystallinity.<sup>21,22</sup> This method aims to reduce defects in the host material. Another method is introducing a sensitizer ion: for example, Yb<sup>3+</sup>, Cr<sup>3+</sup>, etc. Energy transfer efficiency from Cr<sup>3+</sup> to Tm<sup>3+</sup> is 91.7%.<sup>23</sup> However, the absorption of Cr<sup>3+</sup> (400–700 nm) does not match with the commercial GaAlAs pump source (~800 nm). Yb<sup>3+</sup> is the most studied sensitizer for Tm<sup>3+</sup>. Energy transfers from Tm<sup>3+</sup> <sup>3</sup>H<sub>4</sub> to Yb<sup>3+</sup> <sup>2</sup>F<sub>5/2</sub> and then back to Tm<sup>3+</sup> <sup>3</sup>H<sub>5</sub> is observed.<sup>24</sup> This constructs a Tm<sup>3+</sup>  $\rightarrow$  Yb<sup>3+</sup>  $\rightarrow$  Tm<sup>3+</sup> forward–backward energy transfer (FBET) process.<sup>25</sup> An increased <sup>3</sup>F<sub>4</sub> emission with respect to <sup>3</sup>H<sub>4</sub>  $\rightarrow$  <sup>3</sup>F<sub>4</sub> emission of Tm<sup>3+</sup> was observed when it was codoped with Yb<sup>3+</sup>. However, this energy transfer process (normal downconversion luminescence) is less efficient in comparison to the CR process (quantum cutting luminescence). Thus, the absolute <sup>3</sup>F<sub>4</sub> emission (~2 µm) of Tm<sup>3+</sup> was decreased.<sup>26</sup>

The Er<sup>3+</sup> ion has drawn our attention. The  ${}^{4}I_{15/2} \rightarrow {}^{4}I_{13/2}$ transition of Er<sup>3+</sup> shows no energy mismatch with  ${}^{3}H_4 \rightarrow {}^{3}F_4$  of Tm<sup>3+</sup>. Thus, energy transfers from Tm<sup>3+</sup>  ${}^{3}H_4$  to Er<sup>3+</sup>  ${}^{4}I_{13/2}$  and then back-transfers to Tm<sup>3+</sup>  ${}^{3}F_4$  are expected. This is a Tm<sup>3+</sup>  $\rightarrow$ Er<sup>3+</sup>  $\rightarrow$  Tm<sup>3+</sup> FBET system. Although there have been many studies on Tm<sup>3+</sup>- and Er<sup>3+</sup>-codoped systems,<sup>27-29</sup> the FBET

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Figure 1. Rietveld refinement plot of  $Lu_2O_3$  samples. Observed (red cross), calculated (black line), and difference profiles (blue line) of the XRD pattern are plotted in the same range. Bragg peak positions are shown as vertical bars. The coordination environments of Lu1 and Lu2 are shown at the right.

Table 1. C	Cell Parameters and	Coordination	Environments	of Er <sup>3+</sup> -	- and Tm <sup>3</sup>	+-Doped Lu <sub>2</sub>	<b>D</b> <sub>3</sub> Samples
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sample	a (Å)	eccentric distance of Lu1 (Å)	Lu1–O distance (Å)	sphericity of Lu1	eccentric distance of Lu2 (Å)	Lu2–O distance (Å)	sphericity of Lu2
Lu <sub>2</sub> O <sub>3</sub>	10.39	0	18.41	0.84	0.28	18.43	0.85
$(Lu_{0.98}Tm_{0.02})_2O_3$	10.39	0	18.41	0.85	0.17	18.43	0.86
$(Lu_{0.97}Tm_{0.02}Er_{0.01})_2O_3$	10.40	0	18.45	0.85	0.23	18.46	0.86

process has not been reported to our knowledge. The former studies mainly focused on the upconversion luminescence properties of  $Er^{3+}$  or  $Tm^{3+}$ .  $Er^{3+}$  and  $Tm^{3+}$  were doped with high concentration (more than 1%) for high upconversion efficiency. In these cases, the interaction between  $Tm^{3+} {}^{3}F_{4} \rightarrow {}^{3}H_{6}$  and  $Er^{3+} {}^{4}I_{11/2} \rightarrow {}^{4}F_{9/2}$  was dominant.<sup>30</sup>

In this paper, we only introduce a trace amount of  $Er^{3+}$  into  $Lu_2O_3$ : 2 atom %  $Tm^{3+}$ . We find that both  $Tm^{3+} \rightarrow Er^{3+}$  forward energy transfer (FET) and  $Er^{3+} \rightarrow Tm^{3+}$  back energy transfer (BET) processes are effective even at very low  $Er^{3+}$  concentration. Simultaneously, other competitive interaction processes are suppressed. This constructs an ideal  $Tm^{3+} \rightarrow Er^{3+} \rightarrow Tm^{3+}$  FBET system to enhance ~2  $\mu$ m emission of  $Tm^{3+}$ . The  $Tm^{3+} \rightarrow Er^{3+} \rightarrow Tm^{3+}$  energy transfer route provides a new possibility to improve the performance of  $Tm^{3+}$  lasers.

## EXPERIMENTAL SECTION

 $Tm^{3+}$  and  $Er^{3+}$ -doped  $Lu_2O_3$  species were synthesized by the precipitation method.  $Lu_2O_3$  (5 N),  $Tm_2O_3$  (5 N), and  $Er_2O_3$  (6 N) were dissolved in dilute nitric acid to give 0.1 M  $Lu(NO_3)_3$ , 0.01 M  $Tm(NO_3)_3$ , and 0.001 M  $Er(NO_3)_3$  solutions. Stoichiometric amounts of  $Lu(NO_3)_3$ ,  $Tm(NO_3)_3$ , and  $Er(NO_3)_3$  solutions were mixed with stirring at room temperature. Ammonia was dropped into the mixed solution afterward. After the mixture was aged for 6 h, the precipitation was separated via centrifugation at a speed of 6000 revolutions per

minute. The precipitate was washed four times with deionized water and dried in an oven at 60  $^{\circ}$ C for 24 h to give the precursor. The precursor was put into a furnace and sintered at 1500  $^{\circ}$ C for 5 h to obtain the sample.

X-ray diffraction (XRD) patterns were collected in a powder diffractometer (Bruker, D8 Focus, Cu K $\alpha$ , 40 kV, 30 mA). The XRD data were collected in the range of  $15-70^{\circ}$  with a step size of  $0.02^{\circ}$ . Rietveld refinement was performed with the FullProf program package. The photoluminescence (PL) and photoluminescence excitation (PLE) spectra were measured with an FLS920 spectrometer (Edinburgh Instruments, U.K.). Near-infrared photoluminescence spectra were measured by a fiber optics optical meter (Ocean Optical, NIRQUEST256-2.5). A 782 nm laser diode was used as the pump source to excite the  ${}^{3}H_{4}$  level of Tm<sup>3+</sup>. In lifetime measurements, a 10 ns pulsed laser with tunable wavelengths from an optical parametric oscillator (OPO) pumped by a Nd<sup>3+</sup>:YAG laser (Spectra-Physics, GCR 130) was used as a pump source. The signals were detected by a Tektronix digital oscilloscope (TDS 3052). Optical microscope photographs were measured with an Olympus BX53MTRF-S optical microscope. A 980 nm laser diode was used as the light source.

### RESULTS AND DISSCUSSION

Lu<sub>2</sub>O<sub>3</sub> belongs to a cubic lattice with a space group of  $Ia\overline{3}$ . There are two Lu sites in Lu<sub>2</sub>O<sub>3</sub>, namely Lu1 and Lu2, respectively, as shown in Figure 1. The Lu1 site shows an ideal  $S_6$  symmetry, and the Lu2 site shows a distorted  $C_2$  symmetry. Tm<sup>3+</sup> and Er<sup>3+</sup> are considered to be nonluminous in site Lu1



Figure 2. Emission spectra of  $(Lu_{0.98-x}Tm_{0.02}Er_x)_2O_3$  samples excited by 782 nm: (a) measured with an FL920 spectrometer in the range 950–1700 nm; (b) measured with a fiber optics optical meter in the range 1550–2150 nm.

due to its good symmetry. The XRD patterns of pure, Tm<sup>3+</sup>doped, and Tm<sup>3+</sup>- and Er<sup>3+</sup>-codoped Lu<sub>2</sub>O<sub>3</sub> are shown in Figure 1. Rietveld refinement of the XRD patterns was performed. The results show that there is no impure phase. Cell parameters and atom positions were refined for all the samples. The coordination environments of Lu1 and Lu2 were calculated on the basis of the results of Rietveld refinement, as shown in Table 1. The eccentric distance<sup>31</sup> is the distance that the center atom shifts from the centroid of the coordinate atoms. Sphericity estimates the degree that the coordination polyhedron deviates from a sphere. The radii of Tm<sup>3+</sup> and Er<sup>3+</sup> are 0.88 and 0.89 Å, respectively, and are close to that of the Lu<sup>3+</sup> ion (0.861 Å). As shown in Table 1, cell parameters and site coordination of Tm<sup>3+</sup>- and Er<sup>3+</sup>-doped Lu<sub>2</sub>O<sub>3</sub> do not show obvious distortion. This indicates that Tm<sup>3+</sup> and Er<sup>3+</sup> do not change the thermal conductivity of Lu<sub>2</sub>O<sub>3</sub> greatly. This is beneficial for high-power laser applications.

Figure 2 is the emission spectra of  $(Lu_{0.98-x}Tm_{0.02}Er_x)_2O_3$ samples with different concentrations of Er<sup>3+</sup>. Subject to the detection range of different spectrometers, we measured the emission spectra with both a fiber optics spectrometer (Figure 2b) and an FLS920 spectrometer (Figure 2a). As shown in Figure 2, emission peaks from 980 to 1035 nm originate from the  ${}^{4}I_{11/2}$  level of  $Er^{3+}$ . Emission peaks in the range of 1400-1580 nm originate from the  ${}^{3}H_{4} \rightarrow {}^{3}F_{4}$  transition of Tm<sup>3+</sup>. The emission peak at 1537 nm originates from the  ${}^4\mathrm{I}_{13/2}$  level of Er<sup>3+</sup>. Emission peaks from 1600 to 2010 nm originate from the <sup>3</sup>F<sub>4</sub> level of Tm<sup>3+</sup>. As shown in Figure 2a,  $(Lu_{0.9795}Tm_{0.02}Er_{0.0005})_2O_3$  shows the maximum emission intensity of  $Tm^{3+} {}^{3}F_{4}$  with an increased percentage of 41.9%. Further increase in Er<sup>3+</sup> concentration decreases the emission intensity of the  $Tm^{3+} {}^{3}F_{4}$  level. The emission intensity of  $(Lu_{0.978}Tm_{0.02}Er_{0.002})_2O_3$  is even weaker than that of  $(Lu_{0.98}Tm_{0.02})_2O_3$ . As shown in Figure 2a, emission peaks of  $Er^{3+}~^4I_{11/2}$  and  $^4I_{13/2}$  are observed on excitation by a 782 nm laser. The emission intensity increases with higher  $Er^{3+}$  concentration. Since  $Er^{3+}$  cannot be excited by 782 nm light, the luminescence of  $Er^{3+}$  is ascribed to the energy that was transferred from  $Tm^{3+}$ .

Figure 3 is the excitation spectra of  $(Lu_{0.975}Tm_{0.02}Er_{0.005})_2O_3$  monitoring at 980 nm  $(Er^{3+}\ ^4I_{11/2})$  and 1537 nm  $(Er^{3+}\ ^4I_{13/2})$ , respectively. The excitation spectra at both 980 and 1537 nm consist of peaks originating from  $Tm^{3+}$ . This confirms the



**Figure 3.** Excitation spectra of  $(Lu_{0.975}Tm_{0.02}Er_{0.005})_2O_3$  monitored at 980 nm (<sup>4</sup>I<sub>11/2</sub> of Er<sup>3+</sup>, black) and 1537 nm (<sup>4</sup>I<sub>13/2</sub> of Er<sup>3+</sup>, red), respectively. A diagram of the Tm<sup>3+</sup>  $\rightarrow$  Er<sup>3+</sup> energy transfer process is shown at the top right corner.

energy transfer from  $\text{Tm}^{3+}$  to  $\text{Er}^{3+} {}^{4}\text{I}_{11/2}$  and  ${}^{4}\text{I}_{13/2}$  levels. Figure 4 gives the decay curves that monitor the  $\text{Tm}^{3+} {}^{3}\text{H}_{4}$  level. The



Figure 4. Decay curves of  $(Lu_{0.98-x}Tm_{0.02}Er_x)_2O_3$  excited at 684 nm  $({}^{3}F_{2,3} \text{ of }Tm^{3+})$  and monitored at 812 nm  $({}^{3}H_4 \text{ of }Tm^{3+})$  emission.

decay rate is accelerated with increasing  $\mathrm{Er}^{3+}$  concentration. This improves the energy transfer from the  $\mathrm{Tm}^{3+}$   ${}^{3}\mathrm{H}_{4}$  level to  $\mathrm{Er}^{3+}$ . Energy transfer from  $\mathrm{Tm}^{3+}$   ${}^{1}\mathrm{D}_{2}$  and  ${}^{1}\mathrm{G}_{4}$  to  $\mathrm{Er}^{3+}$  have nothing to do with the enhanced ~2  $\mu$ m emission on excitation by a 782 nm laser. In this paper, we only discuss energy transfer processes from the  $\mathrm{Tm}^{3+}$   ${}^{3}\mathrm{H}_{4}$  (can be excited by a 782 nm pump laser) and/or  ${}^{3}\mathrm{F}_{2,3}$  (giving electrons to the  ${}^{3}\mathrm{H}_{4}$  level by nonradiative transition) levels to  $\mathrm{Er}^{3+}$ .

As shown in Figure 3, the intensity of energy levels originating from Er3+ are almost the same for 980 and 1537 nm emission. This is reasonable for a down conversion luminescence. However, the excitation intensity originated from Tm<sup>3+</sup> monitoring 1537 nm is much stronger than that monitoring 980 nm. Energy transfer rates from Tm<sup>3+</sup> to Er<sup>3+</sup>  ${}^{4}I_{13/2}$  and  ${}^{4}I_{11/2}$  levels are different. As shown at the top right corner of Figure 3, there are two possible energy transfer routes from the Tm<sup>3+</sup>  ${}^{3}H_{4}$  or  ${}^{3}F_{2,3}$  level to Er<sup>3+</sup>: one is from the  ${}^{3}H_{4} \rightarrow$  ${}^{3}\text{H}_{6}$  transition of Tm<sup>3+</sup> to  ${}^{4}\text{I}_{15/2} \rightarrow {}^{4}\text{I}_{11/2}$  of Er<sup>3+</sup> (process 0, Figure 3). Another is from the  ${}^{3}\text{H}_{4} \rightarrow {}^{3}\text{F}_{4}$  transition of Tm<sup>3+</sup> to  ${}^{4}I_{15/2} \rightarrow {}^{4}I_{13/2}$  of  $Er^{3+}$  (process 2), Figure 3). Process ① increases in intensity at 980 nm, and process 2 increases in intensity at 1537 nm. Excitation intensity corresponding to the  $Tm^{3+3}F_{2,3}$  level at 1537 nm is 3.6 times that at 980 nm. This indicates that the energy on the Tm<sup>3+ 3</sup>F<sub>2,3</sub> level mostly transfers to Er<sup>3+</sup> <sup>4</sup>I<sub>13/2</sub>. The energy transfer process from the  $Tm^{3+3}H_4 \rightarrow {}^3F_4$  transition to the  $Er^{3+4}I_{13/2}$  level (process 2), Figure 3) is responsible for this phenomenon. Thus, energy transfer from  $Tm^{3+3}H_4 \rightarrow {}^{3}F_4$  to  $Er^{3+4}I_{13/2}$  (process 2), Figure 3) is dominant.

Figure 5 gives the emission spectra of  $(Lu_{0.979}Tm_{0.02}Er_{0.001})_2O_3$  (red) and  $(Lu_{0.999}Er_{0.001})_2O_3$  (black). There are two emission bands of  $Er^{3+}$ : the emission peak at 980–1035 nm originates from the  ${}^{4}I_{11/2}$  level, and the emission peak at around 1537 nm originates from the  ${}^{4}I_{13/2}$  level. The emission intensity of the  $Er^{3+} {}^{4}I_{13/2}$  level is much stronger than that of the  ${}^{4}I_{11/2}$  level for  $(Lu_{0.999}Er_{0.001})_2O_3$ . However, the emission intensity of the  ${}^{4}I_{13/2}$  level is weaker than that of the  ${}^{4}I_{11/2}$  level for  $(Lu_{0.999}Er_{0.001})_2O_3$ . The gray shadow in



Figure 5. Emission spectra of  $(Lu_{0.979}Tm_{0.02}Er_{0.001})_2O_3$  (red) and  $(Lu_{0.999}Er_{0.001})_2O_3$  (black) excited at 782 and 650 nm, respectively. A diagram of the  $Tm^{3+} \rightarrow Er^{3+} \rightarrow Tm^{3+}$  FBET process is shown at the top left corner.

Figure 5 shows the intensity difference. A comparison of the two samples suggests that the difference should be triggered by codoped Tm<sup>3+</sup>. The intensity difference should be caused by energy transfer from  $\text{Er}^{3+} \, {}^{4}\text{I}_{13/2}$  to Tm<sup>3+</sup>. Judging from the energy level diagram (process ②, Figure 5), only the energy of the Tm<sup>3+</sup>  ${}^{3}\text{F}_{4}$  level is close to that of  $\text{Er}^{3+} \, {}^{4}\text{I}_{13/2}$ . Thus, we suppose that the energy transfer route is from  $\text{Er}^{3+} \, {}^{4}\text{I}_{13/2}$  to Tm<sup>3+</sup>  ${}^{3}\text{F}_{4}$ . This can be further confirmed by the following analysis. For example, the emission of Tm<sup>3+</sup>  ${}^{3}\text{F}_{4}$  can be observed when only exciting  $\text{Er}^{3+} \, {}^{4}\text{I}_{11/2}$  (Figure 7) and/or  ${}^{4}\text{I}_{13/2}$  (Figure 8a).

The above analysis constructs a  $\text{Tm}^{3+} \rightarrow \text{Er}^{3+} \rightarrow \text{Tm}^{3+}$  forward–backward energy transfer (FBET) system, as shown at the top left corner of Figure 5 (processes ① and ②). On excitation by 782 nm pump light, energy transfer from the  $\text{Tm}^{3+}{}^{3}\text{H}_{4} \rightarrow {}^{3}\text{F}_{4}$  transition to  $\text{Er}^{3+}{}^{4}\text{I}_{13/2}$  occurs (forward energy transfer, FET). Then, the energy transfers back to the  $\text{Tm}^{3+}{}^{3}\text{F}_{4}$  level from  $\text{Er}^{3+}{}^{4}\text{I}_{13/2}$  (backward energy transfer, BET). This process creates two  $\text{Tm}^{3+}$  ions in the excited  ${}^{3}\text{F}_{4}$  state. In other words, this is a quantum cutting process.

In Tm<sup>3+</sup>- and Er<sup>3+</sup>-codoped samples, the Tm<sup>3+</sup>  $\rightarrow$  Er<sup>3+</sup>  $\rightarrow$  Tm<sup>3+</sup> FBET process and Tm<sup>3+</sup>  $\rightarrow$  Tm<sup>3+</sup> CR process exist simultaneously. For Tm<sup>3+</sup>  $\rightarrow$  Er<sup>3+</sup> and Tm<sup>3+</sup>  $\rightarrow$  Tm<sup>3+</sup> energy transfer processes, the decay curve can be expressed by the Inokuti–Hirayama formula<sup>32,33</sup>

$$I_{\rm d} = I_0 \, \exp\left[-\frac{4}{3}\pi\Gamma\left(1-\frac{3}{s}\right)N_{\rm a}\alpha^{3/s}t^{3/s}\right] \tag{1}$$

where  $I_d$  represents the decay curve of the donor and  $I_0$  represents the decay curve of the donor in the absence of an acceptor. For the  $\text{Tm}^{3+} \rightarrow \text{Tm}^{3+}$  CR process,  $I_d$  is the decay curve of  $(\text{Lu}_{0.98}\text{Tm}_{0.02})_2\text{O}_3$  monitored at 812 nm  $({}^3\text{H}_4 \text{ level})$  emission.  $I_0$  is the decay curve of  $(\text{Lu}_{0.9999}\text{Tm}_{0.0001})_2\text{O}_3$  monitored at 812 nm emission. *s* is a coefficient with values of 6, 8, and 10, respectively, for dipole–dipole, dipole–quadrupole, and quadrupole–quadrupole interactions.  $N_a$  is the number of acceptor ions per unit volume. It can be derived that  $\log\{-\ln[I_d/I_0]\}$  shows a linear dependence on  $\log t$  with a slope of 3/s. As shown in Figure 6a, *s* can be calculated to be 4.3, close to 6. Thus, the electric interaction type of the  $\text{Tm}^{3+} \rightarrow \text{Tm}^{3+}$  CR process is dipole–dipole.

For the  $Tm^{3+} \rightarrow Er^{3+}$  forward energy transfer (FET) process,  $I_d$  is the decay curve of  $(Lu_{0.979}Tm_{0.02}Er_{0.001})_2O_3$  monitored at



Figure 6. (a, c) Relationship between  $\log[-\ln(I(t)/I_0(t))]$  and  $\log t$  of  $(Lu_{0.98}Tm_{0.02})_2O_3$  and  $(Lu_{0.979}Tm_{0.02}Er_{0.001})_2O_3$ . (b, d) Plots of  $\ln[I(t)/I_0(t)]$  vs  $t^{1/2}$  for  $(Lu_{0.98}Tm_{0.02})_2O_3$  and  $(Lu_{0.979}Tm_{0.02}Er_{0.001})_2O_3$ .

812 nm.  $I_0$  is the decay curve of  $(Lu_{0.98}Tm_{0.02})_2O_3$  monitored at 812 nm. As shown in Figure 6c, *s* can be calculated to be 5.4, also close to 6. Thus, the electric interaction type from Tm<sup>3+</sup>  ${}^{^3}H_4 \rightarrow {}^{^3}F_4$  to  $Er^{3+} {}^{^4}I_{13/2}$  is also dipole–dipole.

The critical energy transfer distance  $R_0$  is the distance between an isolated donor–acceptor pair where the energy transfer rate is the same with the spontaneous radiation of the donor.  $R_0$  can be calculated by the formula  $R_0^6 = \alpha \tau_0$ .  $\alpha$  is a rate constant for energy transfer and can be calculated through a transformed Inokuti–Hirayama formula:

$$\ln \frac{I_{\rm d}}{I_0} = -\frac{4}{3}\pi \Gamma \left(\frac{1}{2}\right) n_{\rm A} \alpha^{1/2} t^{1/2} \tag{2}$$

As shown in Figure 6c,d,  $\alpha$  values for the Tm<sup>3+</sup>  $\rightarrow$  Tm<sup>3+</sup> CR process and the Tm<sup>3+</sup>  $\rightarrow$  Er<sup>3+</sup> FET process equal 8.476  $\times$  10<sup>-40</sup> and 5.868  $\times$  10<sup>-37</sup> cm<sup>6</sup> s<sup>-1</sup> respectively.  $\tau_0$  for the Tm<sup>3+</sup>  $\rightarrow$  Tm<sup>3+</sup> CR process is 346  $\mu$ s, which is obtained by integrating the decay curve of (Lu<sub>0.9999</sub>Tm<sub>0.0001</sub>)<sub>2</sub>O<sub>3</sub>.  $\tau_0$  for the FET process is 77  $\mu$ s and is obtained from the decay of (Lu<sub>0.98</sub>Tm<sub>0.02</sub>)<sub>2</sub>O<sub>3</sub>. Thus,  $R_0$  values are calculated to be 8.15 and 18.88 Å for the Tm<sup>3+</sup>  $\rightarrow$  Tm<sup>3+</sup> CR process and Tm<sup>3+</sup>  $\rightarrow$  Er<sup>3+</sup> FET process, respectively.

The critical concentration  $C_0$  is the concentration at which the energy transfer rate is equal to the spontaneous radiation rate. Critical concentration can be calculated by the formula

$$C_0 = \frac{3}{4\pi N_a R_0^{\ 3}}$$
(3)

Thus, the  $C_0$  value of the  $\text{Tm}^{3+} \rightarrow \text{Tm}^{3+}$  CR process is calculated to be 0.0155 and the  $C_0$  value of the  $\text{Tm}^{3+} \rightarrow \text{Er}^{3+}$  FET process is calculated to be 0.0012. This indicates that the

 $Tm^{3+} \to Er^{3+}$  FET process works efficiently even at very low  $Er^{3+}$  concentration.

For the  $Er^{3+} \rightarrow Tm^{3+}$  back energy transfer (BET) process, energy transfer efficiency can be estimated by

$$\eta_{\rm BET} = 1 - \frac{I}{I_0} \tag{4}$$

where  $I_0$  is the emission intensity of the donor without an acceptor and *I* is the emission intensity with an acceptor. Figure 7 gives the emission spectra of  $(Lu_{0.979}Tm_{0.02}Er_{0.001})_2O_3$  and  $(Lu_{0.98}Tm_{0.02})_2O_3$  excited at 980 nm. The emission intensity of



Figure 7. Emission spectra of  $(Lu_{0.975}Tm_{0.02}Er_{0.001})_2O_3$  (red) and  $(Lu_{0.98}Tm_{0.02})_2O_3$  (black) excited at 980 nm.

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Figure 8. (a) Emission spectra of  $(Lu_{0.98-x}Tm_{0.02}Er_x)_2O_3$  excited at 1450 nm. (b) Ratio of 1633 nm ( ${}^{3}F_4$  of  $Tm^{3+}$ ) to 1537 nm ( ${}^{4}I_{13/2}$  of  $Er^{3+}$ ). (c) Diagram of  $Er^{3+} \leftrightarrow Tm^{3+}$  reciprocating transfer process.

 $\mathrm{Er}^{3^+}{}^{3}\mathrm{I}_{11/2}$  shows a sudden decrease with codoped Tm<sup>3+</sup>. Back energy transfer efficiency,  $\eta_{\mathrm{BET}}$ , can be calculated with eq 4, and the value is 99.54%. The  $\mathrm{Er}^{3^+} \rightarrow \mathrm{Tm}^{3^+}$  BET process is highly efficient at low  $\mathrm{Er}^{3^+}$  concentration. The high energy transfer efficiency is interpreted by high Tm<sup>3+</sup> concentration.

The above analysis indicates that the Tm<sup>3+</sup>  $\rightarrow$  Er<sup>3+</sup>  $\rightarrow$  Tm<sup>3+</sup> FBET system works efficiently even at very low Er<sup>3+</sup> concentration. For the Tm<sup>3+</sup>  $\rightarrow$  Tm<sup>3+</sup> CR process, a high concentration of Tm<sup>3+</sup> is necessary. However, high Tm<sup>3+</sup> concentration results in energy migration between Tm<sup>3+</sup> ions. If the energy migrates to a Tm<sup>3+</sup> ion with defects around it, the luminescence is quenched. When an Er<sup>3+</sup> ion is introduced, the Tm<sup>3+</sup>  $\rightarrow$  Er<sup>3+</sup> FET process competes with the energy migration process. Thus, Er<sup>3+</sup> ion recycles a certain proportion of quenching energy. The recycled energy is given back to the Tm<sup>3+</sup> ion by the Er<sup>3+</sup>  $\rightarrow$  Tm<sup>3+</sup> BET process. This process reduces energy migration between <sup>3</sup>H<sub>4</sub> levels of Tm<sup>3+</sup> and increases the emission intensity of Tm<sup>3+</sup> <sup>3</sup>F<sub>4</sub> level (~2  $\mu$ m).

Figure 8a gives the emission spectra of  $(Lu_{0.98-x}Tm_{0.02}Er_x)_2O_3$  excited at 1450 nm, which only excites the  ${}^{4}I_{13/2}$  level of  $Er^{3+}$ . Emission of  ${}^{3}F_4$  (1633 nm) of  $Tm^{3+}$  is observed in Figure 8a. This confirms the energy transfer process from  $Er^{3+} {}^{4}I_{13/2}$  to  $Tm^{3+} {}^{3}F_4$ . However, the intensity ratio of  $Tm^{3+} {}^{3}F_4$  to  $Er^{3+} {}^{4}I_{13/2}$  decreases rapidly with increasing  $Er^{3+}$  concentration, as shown in Figure 8b. This is because the energy at the  $Tm^{3+} {}^{3}F_4$  level may transfers back to the  $Er^{3+} {}^{4}I_{13/2}$  level by thermal disturbance. As shown in Figure 8c, the  ${}^{4}I_{13/2}$  level of  $Er^{3+}$  is 6313 cm<sup>-1</sup>, as estimated from the emission spectrum, and the  ${}^{3}F_4$  level of  $Tm^{3+}$  is estimated to be 5186 cm<sup>-1</sup>. The energy difference is 1127 cm<sup>-1</sup> and is only about two phonons of  $Lu_2O_3$  (618 cm<sup>-1</sup>). This process becomes obvious at higher  $Er^{3+}$  concentration. Thus, ~2  $\mu$ m emission of  $Tm^{3+}$  decreases with higher  $Er^{3+}$  concentration. Enhanced emission of  $Tm^{3+}$  can only be observed at a low concentration of  $Er^{3+}$ .

Another energy transfer process that may quench the ~2  $\mu$ m emission is from Tm<sup>3+</sup>  ${}^{3}F_{4} \rightarrow {}^{3}H_{6}$  to  $Er^{3+} {}^{4}I_{11/2} \rightarrow {}^{4}F_{9/2}$ , as shown in Figure 9. The upconversion spectra of  $(Lu_{0.97}Tm_{0.02}Er_{0.01})_{2}O_{3}$  and  $(Lu_{0.99}Er_{0.01})_{2}O_{3}$  excited at 980



Figure 9. Upconversion spectra of  $(Lu_{0.97}Tm_{0.02}Er_{0.01})_2O_3$  and  $(Lu_{0.99}Er_{0.01})_2O_3$  excited at 980 nm. The color maps are the optical microscope photographs (500×) of  $(Lu_{0.97}Tm_{0.02}Er_{0.01})_2O_3$  and  $(Lu_{0.99}Er_{0.01})_2O_3$  at 980 nm. The energy scheme shows the green and red upconversion process.

nm are quite different. For  $(Lu_{0.99}Er_{0.01})_2O_3$ , the upconversion color is mainly green, while that for  $(Lu_{0.97}Tm_{0.02}Er_{0.01})_2O_3$  is red. The green emission originates from the  ${}^{2}H_{11/2}$  and  ${}^{4}S_{3/2}$  levels of  $Er^{3+}$ . The two levels are populated by a sequential two photon absorption  ${}^{4}I_{15/2} \rightarrow {}^{4}I_{11/2}$  and  ${}^{4}I_{11/2} \rightarrow {}^{4}F_{7/2}$ , as shown in the energy scheme in Figure 9. This process is well-known for normal upconversion luminescence. When  $Tm^{3+}$  is introduced, red emission from  ${}^{4}F_{9/2}$  of  $Er^{3+}$  dominates. A new energy transfer process from  ${}^{3}F_4 \rightarrow {}^{3}H_6$  of  $Tm^{3+}$  to  ${}^{4}I_{11/2} \rightarrow {}^{4}F_{9/2}$  of  $Er^{3+}$  occurs. When the  ${}^{4}I_{11/2}$  level of  $Er^{3+}$  is populated by a 980 nm laser, process ① populates the  ${}^{3}F_4$  level of  $Tm^{3+}$ . This process is shown in the diagram in Figure 9. Process ② decreases the emission intensity of the  $Tm^{3+} {}^{3}F_4$  level ( $\sim 2 \mu m$ ).

## CONCLUSIONS

A trace amount of  $\rm Er^{3+}$  is introduced into  $\rm Lu_2O_3{:}Tm^{3+}.$  Site distortion is quantified to show the influence of  $\rm Er^{3+}$  and  $\rm Tm^{3+}$ 

to Lu sites. No obvious distortion is observed. This is important for high-power laser applications. The emission intensity of  $Tm^{3+}$  is enhanced with a low concentration of  $Er^{3+}$ . A new  $Tm^{3+} \rightarrow Er^{3+} \rightarrow Tm^{3+}$  FBET system is proved in this paper. The energy transfers from the  $Tm^{3+3}H_4$  level to the  $Er^{3+4}I_{13/2}$ level and then back-transfers to the  $Tm^{3+3}F_4$  level. The  $Tm^{13}$  $\rightarrow Er^{3+} \rightarrow Tm^{3+}$  FBET is a quantum cutting process and works efficiently at very low  $Er^{3+}$  concentration. The critical concentration for the  $Tm^{3+} \rightarrow Er^{3+}$  forward energy transfer process (FET) is 0.0012. This value is much smaller than that of the  $Tm^{3+} \rightarrow Tm^{3+}$  CR process (0.0155). For the  $Er^{3+} \rightarrow$ Tm<sup>3+</sup> back energy transfer process, the energy transfer efficiency reaches 99.54%. With higher Er<sup>3+</sup> concentration, other energy transfer processes are observed between Tm<sup>3+</sup> and  $Er^{3+}$  to decrease the ~2  $\mu m$  emission of  $Tm^{3+}$ . Thus, a trace amount of  $Er^{3+}$  not only constructs an efficient  $Tm^{3+} \rightarrow Er^{3+} \rightarrow$ Tm<sup>3+</sup> FBET system but also suppresses quenching energy transfer processes. As the result, the  $\sim 2 \,\mu m$  emission of Tm<sup>3+</sup> is enhanced.

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Notes

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