

## Efficient up-converted white emission in $\text{Er}^{3+}$ , $\text{Tm}^{3+}$ and $\text{Yb}^{3+}$ tridoped $\text{NaYF}_4$ powders

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Much interest has been motivated in the conversion of near infrared radiation into visible light in rare earth doped materials because of its potential applications, such as color display, optical data storage, biomedical diagnostics, sensors, under sea optical communications [1–5]. More recently, white up-conversion emission has especially attracted much attention due to its wide variety of applications, from compact light source to photonic devices [6]. For quite some time,  $\text{NaYF}_4$  host lattice has been recognized as one of the most efficient up-conversion lattices [7–9]. Efficient up-converted green and blue emission has been previously reported in  $\text{Er}^{3+}$ ,  $\text{Yb}^{3+}$  co-doped and  $\text{Tm}^{3+}$ ,  $\text{Yb}^{3+}$  co-doped  $\text{NaYF}_4$  matrix, respectively [7–10]. However, no white emission is reported in this efficient host. In this paper, we will report an up-conversion in  $\text{Er}^{3+}$ ,  $\text{Tm}^{3+}$  and  $\text{Yb}^{3+}$  co-doped  $\text{NaYF}_4$  powder. In this material doped with three kinds of rare earth ions, intense multicolor up-converted emission has been observed. It has also been proved that the intensity of up-conversion emission can be adjusted by changing the doping concentration. More noticeably, bright white luminescence has been realized in

this  $\text{Er}^{3+}$ ,  $\text{Tm}^{3+}$  and  $\text{Yb}^{3+}$  co-doped  $\text{NaYF}_4$  powder for the first time.

The rare earth doped  $\text{NaYF}_4$  powder was synthesized using the conventional solid-state interaction method. The raw compositions in molar ratio are  $1\text{NaF}-(0.745-x)\text{YF}_3-x\text{ErF}_3-0.005\text{TmF}_3-0.25\text{YbF}_3$ , with  $x = 0.01, 0.02, 0.03, 0.04$  and  $0.06$ . Having been mixed and grounded thoroughly, the raw reagents were poured into crucibles, heated to  $900^\circ\text{C}$  with a rate of  $20^\circ\text{C}/\text{min}$ . After keeping at that temperature for 1 h, the powders were cooled to room temperature with a rate of  $1^\circ\text{C}/\text{min}$ . All these processes were all carried out under HF atmosphere. For the convenience of following description, the samples with original molar composition of  $1\text{NaF}-(0.745-x)\text{YF}_3-x\text{ErF}_3-0.005\text{TmF}_3-0.25\text{YbF}_3$  with  $x = 0.01, 0.02, 0.03, 0.04$  and  $0.06$  are respectively named as NYF1, NYF2, NYF3, NYF4, NYF6, respectively.

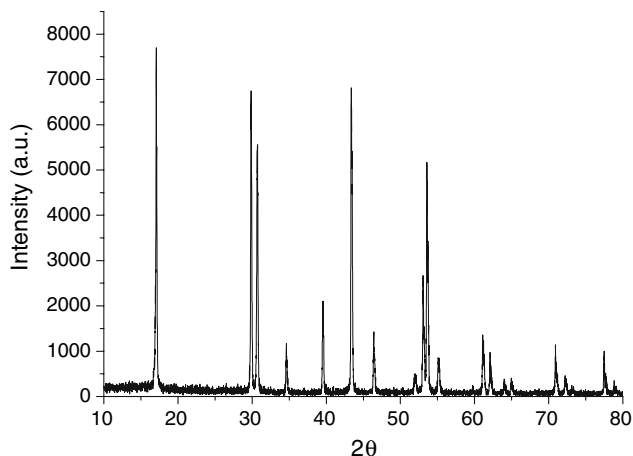
The crystalline phases of the samples were identified by X-ray diffraction. The X ray patterns were obtained using a D/Max-EAX equipment provided with a Cu tube with Ka radiation at 1.5405 Å, scanning in the  $10-80 2\theta$  range with 0.02 increments. Figure 1 shows the XRD pattern of the sample with  $\text{Er}^{3+}$  concentration of 1%. It shows a typical hexagonal structure and basically accords with the standard X-ray diffraction JCPDS 16-0334. The XRD patterns for other samples doped with different  $\text{Er}^{3+}$  concentration are similar. It suggests that all the samples crystallized into  $\beta\text{-NaY}_{(0.745-x)}\text{Er}_x\text{Yb}_{0.25}\text{Tm}_{0.005}\text{F}_4$  ( $x = 0.01, 0.02, 0.03, 0.04$  and  $0.06$ ) with hexagonal structure, in which  $\text{Y}^{3+}$  ions are partly substituted by  $\text{Er}^{3+}$ ,  $\text{Tm}^{3+}$  and  $\text{Yb}^{3+}$  ions.

The up-conversion luminescence in these samples is so intense as to be seen by naked eyes at excitation power density as low as  $20 \text{ mw}/\text{mm}^2$ . A photomultiplier tube coupled spectrometer was used to record the up-converted

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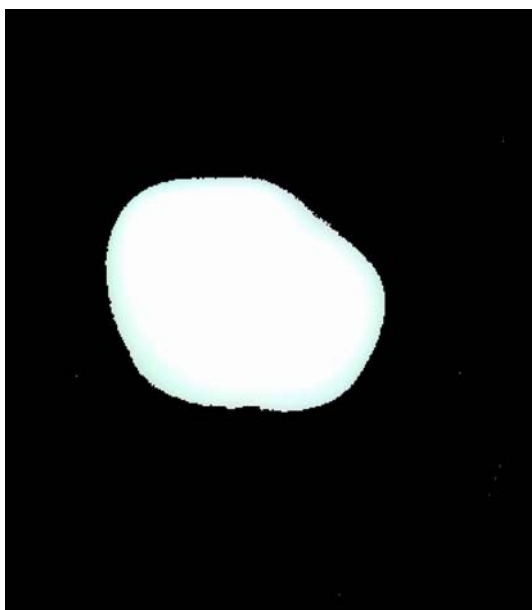
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**Fig. 1** X ray diffraction pattern of the NYF1 sample

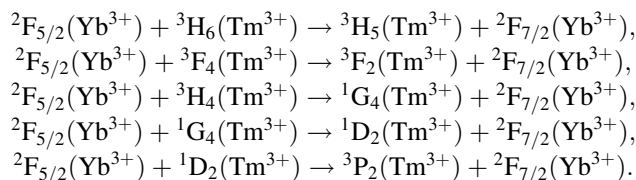
luminescence spectra at room temperature. Figure 2 presents the photograph of up-conversion of the NYF1 sample under a 980 nm diode light with power density of 150 mw/mm<sup>2</sup>. Intense bright white luminescence has been observed under the near infrared excitation. Figure 3 shows the up-conversion spectra of the NYF1 sample upon 980 nm laser excitation. Eleven up-converted emission bands at 346, 361, 410, 451, 478, 524, 541, 655, 694, 725 and 802 nm, have been observed.

According to energy level diagram of Tm<sup>3+</sup> [11], the up-converted emissions at 346, 361, 451, 478, 694, 725 and 802 nm may be assigned to the <sup>1</sup>I<sub>6</sub> → <sup>3</sup>F<sub>4</sub>, <sup>1</sup>D<sub>2</sub> → <sup>3</sup>H<sub>6</sub>, <sup>1</sup>D<sub>2</sub> → <sup>3</sup>F<sub>4</sub>, <sup>1</sup>G<sub>4</sub> → <sup>3</sup>H<sub>6</sub>, <sup>3</sup>F<sub>1</sub> → <sup>3</sup>H<sub>6</sub>, <sup>3</sup>F<sub>2</sub> → <sup>3</sup>H<sub>6</sub>,

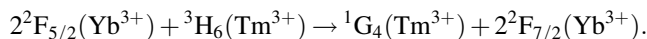


**Fig. 2** Photograph of the NYF1 sample under excitation of 980 nm laser with power density of 150 mw/mm<sup>2</sup>

<sup>3</sup>H<sub>4</sub> → <sup>3</sup>H<sub>6</sub> transitions of Tm<sup>3+</sup>, respectively. The other emissions at 410, 524, 541 and 655 nm can be respectively assigned to the <sup>2</sup>H<sub>9/2</sub> → <sup>4</sup>I<sub>15/2</sub>, <sup>2</sup>H<sub>11/2</sub> → <sup>4</sup>I<sub>15/2</sub>, <sup>4</sup>S<sub>3/2</sub> → <sup>4</sup>I<sub>15/2</sub>, <sup>4</sup>F<sub>9/2</sub> → <sup>4</sup>I<sub>15/2</sub> transitions of Er<sup>3+</sup>. Multiple step energy transfers from Yb<sup>3+</sup> to Tm<sup>3+</sup> might be responsible for the up-converted emissions. These energy transfer processes are



Considering that the energy of the <sup>1</sup>G<sub>4</sub> level of Tm<sup>3+</sup> is almost equal to the sum of two 980 nm photons, a cooperative sensitization process might also be responsible for the population of the <sup>1</sup>G<sub>4</sub> level of Tm<sup>3+</sup> [12]. This mechanism is described as



Similarly, the energy transfer from Yb<sup>3+</sup> to the Er<sup>3+</sup> ions may perform the population of the upper levels of Er<sup>3+</sup>. These energy transfer pathways include

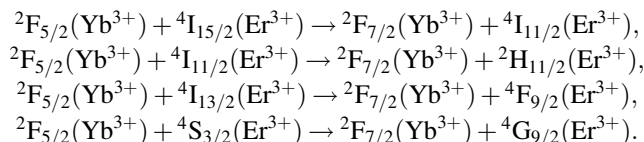
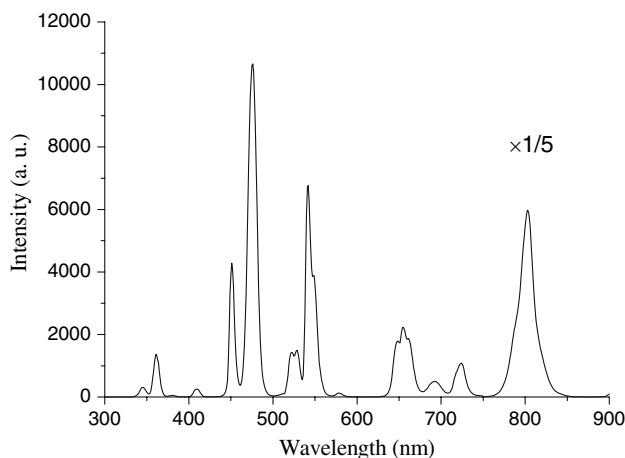
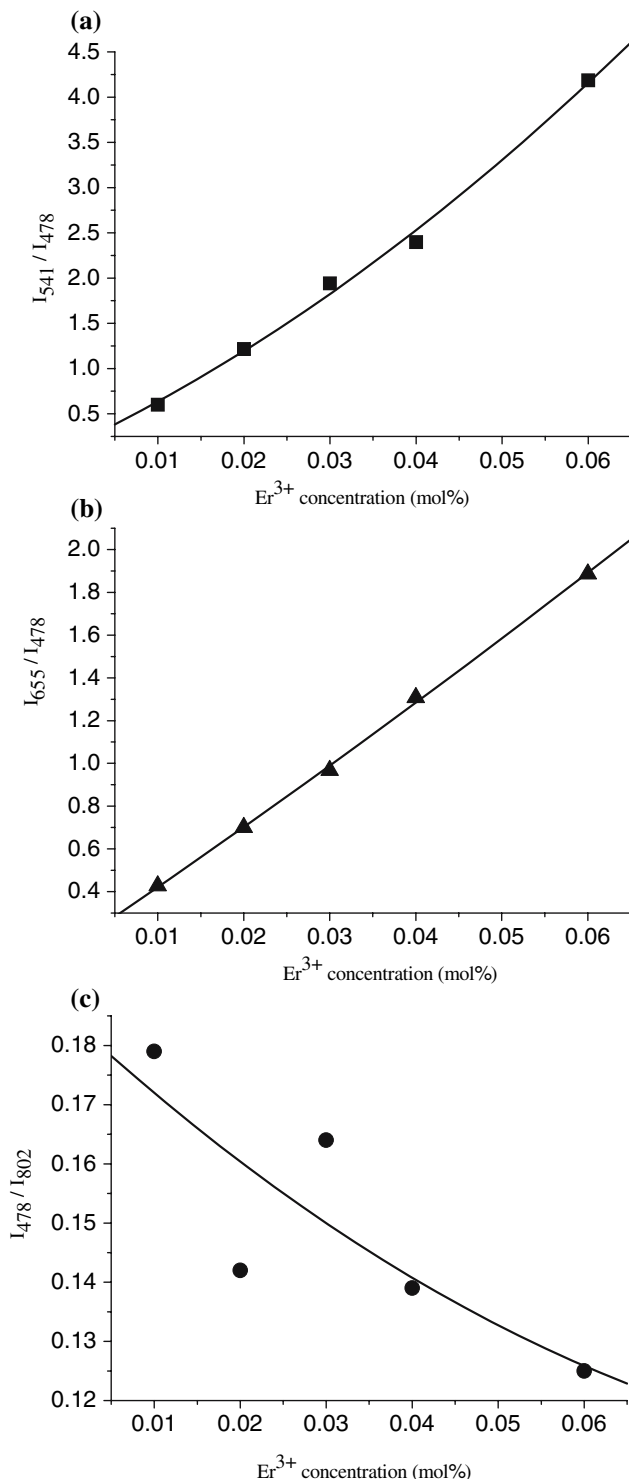


Figure 4 shows the integrated intensity ratio of some transitions as a function of Er<sup>3+</sup>-ion concentration under excitation of 980 nm laser with powder density of



**Fig. 3** Up-converted emission spectra of the NYF1 samples under 980 nm excitation

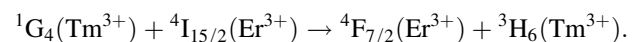


**Fig. 4** Integrated intensity ratio of some transitions against the Er<sup>3+</sup>-ion concentration under excitation of 980 nm laser with power density of 150 mw/mm<sup>2</sup>

150 mw/mm<sup>2</sup>. From Fig. 4(a) and (b), one may find that the integrated intensities of the green and red emissions increase relative to the blue emission at 478 nm with the

increase of the Er<sup>3+</sup>-ion doping concentration. As a matter of fact, the up-conversion luminescence of the sample NYF6, whose doping concentration of Er<sup>3+</sup> reaches to 6%, is no longer white. It is not difficult to understand the enhancement of the green and red luminescence. Since the Er<sup>3+</sup> ion mainly emits the green luminescence at 541 nm and the red luminescence at 655 nm, more Er<sup>3+</sup> will be involved in the up-conversion with the increase of the Er<sup>3+</sup>-ion content. On the other hand, the energy transfer probability from Yb<sup>3+</sup> to Er<sup>3+</sup> ions will also increase with the enhancement of the Er<sup>3+</sup>-ion concentration. As the Er<sup>3+</sup>-ion concentration increases, the space between the sensitizer Yb<sup>3+</sup> and activator Er<sup>3+</sup> will reduce. This will result in the enhancement of the energy transfer probability from Yb<sup>3+</sup> to Er<sup>3+</sup> ions, also leading to the increase of the green and red emission of Er<sup>3+</sup> ions.

In addition, from Fig. 4(c), one may find that the blue emission of Tm<sup>3+</sup> at 478 nm tends decrease relative to its near infrared emission at 802 nm when the Er<sup>3+</sup>-ion concentration increases. Since the doping concentration of Tm<sup>3+</sup> is invariable, the decrease of the emission at 478 nm indicates that the energy transfer between Er<sup>3+</sup> and Tm<sup>3+</sup> ions might occur. A possible mechanism is



Through this process, the particle population of the <sup>1</sup>G<sub>4</sub> level of Tm<sup>3+</sup> may be depleted, resulting in the decrease of the blue emission at 478 nm.

In brief, Er<sup>3+</sup>, Tm<sup>3+</sup> and Yb<sup>3+</sup> tridoped NaYF<sub>4</sub> powders are synthesized. XRD patterns reveal that all the samples with different Er<sup>3+</sup> concentration crystallized into β-NaYF<sub>4</sub> with a hexagonal structure. Multi-color up-converted emission has been observed. With the increase of the Er<sup>3+</sup>-ion doping concentration, the integrated intensities of the green and red emissions increase relative to the blue emission at 478 nm, indicating that the up-conversion emission can be adjusted by changing the doping concentration. More noticeably, bright white luminescence has been realized in the Er<sup>3+</sup>, Tm<sup>3+</sup> and Yb<sup>3+</sup> co-doped NaYF<sub>4</sub> powder for the first time. Multiple step energy transfers from Yb<sup>3+</sup> to Tm<sup>3+</sup> and Er<sup>3+</sup> are responsible for the up-converted emissions, while an energy transfer between Tm<sup>3+</sup> and Er<sup>3+</sup> might also occur.

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