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Study on up-conversion emissions of Yb3+/Tm3+ co-doped GdF3 and NaGdF4

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ABSTRACT

The Yb^{3+}/Tm^{3+} co-doped GdF_3 and $NaGdF_4$ samples were synthesized through a combination method of a co-precipitation and an argon atmosphere annealing procedures. X-ray diffraction analysis indicated that the Yb^{3+}/Tm^{3+} co-doped GdF_3 sample crystallized well and was orthorhombic phase, and the Yb^{3+}/Tm^{3+} co-doped $NaGdF_4$ sample was hexagonal phase. With a 980-nm semiconductor continuous wave laser diode as the excitation source, the up-conversion emission spectra of the two samples in the wavelength range of 240–510 nm were recorded. In the up-conversion emissions of the samples, Yb^{3+} transferred energies to Tm^{3+} resulting in their ultraviolet, violet, and blue up-conversion emissions. And, Tm^{3+} simultaneously transferred energies to Gd^{3+} , which finally resulted in ultraviolet up-conversion emissions of Gd^{3+} . The study on the excitation power dependence of up-conversion fluorescence intensity indicated that there were multi-photon (three-, four-, five-, and six-) processes in the up-conversion emissions of the samples. And the up-conversion emissions of Gd^{3+} and Tm^{3+} in the Tm^{3+} co-doped Tm^{3+} and Tm^{3+} in the Tm^{3+} co-doped Tm^{3+} and Tm^{3+} samples were compared studied, too.

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1. Introduction

Up-conversion (UC) is one of physical mechanisms for varying the frequency of light, where lower energy light, usually nearinfrared (NIR) or infrared (IR), is converted to high energy light, ultraviolet (UV) or visible, via multiple absorption and energy transfer processes, and so on. For the benefits of intrinsic energy levels matching of certain rare earth (RE) ions and the ample availability of laser diodes (LDs) in the visible and IR range, frequency UC is an important process in optical generation within RE-doped materials. RE-doped up-converted materials have been widely studied because of their potential applications, such as optical data storage, color displays, IR sensors, environmental monitoring, and so on [1-5]. For Gd³⁺, its compounds have a wide range of applications. For example, Gd₂SiO₅ [6], Gd₂O₃ [7], LiGdF₄ [8], and GdBO₃ [9], were extensively studied and used, where Gd³⁺ served as host material ions, activator or sensitizer ions. However, UC emissions of Gd3+ are rarely studied for the large energy gap between the ground state ${}^8S_{7/2}$ and the first excited state ${}^6P_{7/2}$ $(\sim 32,000 \text{ cm}^{-1})$. In the Ref. [10], the researchers used green lasers (546 and 522 nm) as pump lights and carried out a cooperative energy transfer (ET) from Er3+ to Gd3+. Recently, Cao et al. firstly reported the ⁶I_I and ⁶P_I states to the ground state ⁸S_{7/2} emissions of Gd³⁺ with a 980-nm LD as the excitation source [11]. Later, Qin et al. reported the 6D_J levels to the $^8S_{7/2}$ level emissions [12]. Subsequently, Chen et al. reported the near vacuum UV (VUV) UC emissions of Gd^{3+} under a 974-nm LD excitation [13]. To the best of our knowledge, there were no UC emission comparisons of Gd^{3+} or Tm^{3+} based on the NaGdF₄ and GdF_3 host materials.

In the article, the 20%Yb³+, 0.7%Tm³+ co-doped GdF₃ and NaGdF₄ samples were synthesized through a co-precipitation method and an annealing procedure. Under a 980-nm semiconductor continuous wave laser diode (CW LD 2 W) excited, the samples presented UC emissions of Gd³+ and Tm³+. In the UC emissions of the samples, Yb³+ transferred energies to Tm³+ resulting in their UV and blue UC emissions. For UV UC emissions of Gd³+, Yb³+ ions serving as primary sensitizer ions and Tm³+ ions simultaneously acting as secondary sensitizer ions continuously transferred energies to Gd³+, which finally resulted in UV UC emissions of Gd³+. The study of excitation power dependence of UC fluorescence intensity of the samples indicated that the UC emissions were three-, four-, five-, or six-photon processes. And the UC emissions of Gd³+ and Tm³+ in the two 20%Yb³+, 0.7%Tm³+ co-doped GdF₃ and NaGdF₄ samples were compared studied, too.

2. Experimental

The $20\%Yb^{3+}$, $0.7\%Tm^{3+}$ co-doped GdF_3 sample was synthesized according to the following procedure. Firstly, 7.93 mmol Gd_2O_3 , 2 mmol Yb_2O_3 , and 0.07 mmol Tm_2O_3 , were dissolved in the dilute hydrochloric acid (HCl) at elevated temperature to form clear

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solution. Then, 30 mmol NH₄HF₂, dissolving in the deionized water, was added dropwise into the clear solution to form turbid liquid while stirring with a magnetic force stirrer. After vigorously stirred for more than 0.5 h, the turbid liquid was washed with the deionized water via centrifugation at least three times. The resultant material was dried in vacuum at 60 °C for 10 h and was annealed in an argon atmosphere at 600 °C for 1 h. The 20%Yb³+, 0.7%Tm³+ co-doped GdF₃ sample was finally obtained. For synthesis of the 20%Yb³+, 0.7%Tm³+ co-doped NaGdF₄ sample, the procedure was same as that of the 20%Yb³+, 0.7%Tm³+ co-doped GdF₃ sample besides adding overmuch NaF (1:1 molar ratio) when annealing under an argon atmosphere.

With nickel-filtered Cu K α radiation (λ = 1.5406 Å), the crystallization phase identification was carried out by X-ray diffraction (XRD) analysis with a powder diffractometer (Model Rigaku RU-200b). UC emission spectra were recorded with a fluorescence spectrophotometer (Hitachi F-4500), using a 980-nm semiconductor CW LD equipped with an object lens (×10) as the excitation source, which was placed about at an angle of 45° before the sample (about 0.2 g held by the sample holder). One should adjust the laser focus point to excite the sample when measuring UC emission spectra. All measurements were performed at room temperature.

3. Results and discussion

Fig. 1 shows XRD patterns of the $20\% Yb^{3+}$, $0.7\% Tm^{3+}$ co-doped GdF₃ unannealed, annealed at $600\,^{\circ}\text{C}$ for 1 h, adding overmuch NaF annealed at $600\,^{\circ}\text{C}$ for 1 h, and the standard data of GdF₃ and NaGdF₄. Compared the experimental data to those published by the Joint Committee on Powder Diffraction Standard (JCPDS) cards, the unannealed $20\% Yb^{3+}$, $0.7\% Tm^{3+}$ co-doped GdF₃ was orthorhombic phase with space group pnma(62) (JCPDS 49-1804). After annealed, the sample crystallized well, which can be concerned from the narrowed peaks of the XRD pattern. For the sample adding NaF when annealing, the data agreed with those of space group P6₃/m (176) (JCPDS 27-0699), indicating that the final resultant sample was hexagonal phase Yb³⁺/Tm³⁺ co-doped NaGdF₄.

Fig. 2 is the energy level diagrams of Gd^{3+} , Yb^{3+} , and Tm^{3+} [14,15], and the possible up-converted processes were plotted in the diagrams, too. In the Tm^{3+} – Yb^{3+} – Gd^{3+} co-existing system with

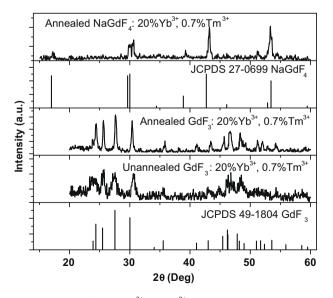


Fig. 1. XRD patterns of the $20\%Yb^{3+}$, $0.7\%Tm^{3+}$ co-doped GdF₃ sample unannealed, annealed at $600\,^{\circ}$ C for 1 h, the $20\%Yb^{3+}$, $0.7\%Tm^{3+}$ co-doped NaGdF₄ sample annealed at $600\,^{\circ}$ C for 1 h, and standard data of GdF₃ and NaGdF₄.

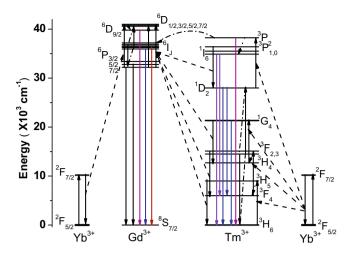


Fig. 2. Scheme energy level diagrams of Yb³⁺, Tm³⁺, Gd³⁺, and possible upconverted processes in the samples.

a 980-nm LD as the excitation source, Yb3+ successively transfer energy to Tm^{3+} to populate their 3H_5 , 3F_3 (3F_2), and 1G_4 levels [16]. For the large energy mismatch (\sim 3500 cm $^{-1}$) in the ET ${}^{2}F_{5/2} \rightarrow {}^{2}F_{7/2} \text{ (Yb}^{3+}): {}^{1}G_{4} \rightarrow {}^{1}D_{2} \text{ (Tm}^{3+}), \text{ the } {}^{1}D_{2} \text{ level cannot be pop-}$ ulated directly through the ET process Alternatively, the ¹D₂ level can be populated through the cross relaxation process $^3F_3 \rightarrow ^3H_6$: $^3F_3 \rightarrow ^1D_2$ (Tm $^{3+}$) [17,18]. The 3P_2 (Tm $^{3+}$) level is populated by the ET $^2F_{5/2} \rightarrow ^2F_{7/2}$ (Yb $^{3+}$): $^1D_2 \rightarrow ^3P_2$ (Tm $^{3+}$) [11]. Some of Tm $^{3+}$ ions in the ³P₂ state make the radiative transition to the ground state ${}^{3}H_{6}$, some of them relax rapidly and nonradiatively to the ${}^{1}I_{6}$ level, and the others transfer energy to 6I_J levels of Gd^{3+} through the ET $^3P_2 \rightarrow ^3H_6$ (Tm $^{3+}$): $^8S_{7/2} \rightarrow ^6I_J$ (Gd $^{3+}$) [11]. At room temperature, the nonradiative relaxation $^6I_J \rightarrow ^6P_J$ leads to the population of $^6P_{5/2}$ and $^6P_{7/2}$ levels efficiently [19]. Then, the 6D_J levels of Gd^{3+} can be populated further. Three mechanisms should be considered in populating 6D_J levels: excited state absorption, cross relaxation between Gd^{3+} , and ET processes between Gd^{3+} and Yb^{3+} or Tm^{3+} [12]. Due to their appropriate energy matching, the ET $^2F_{5/2} \rightarrow$ $^{2}F_{7/2}$ (Yb³⁺): $^{6}P_{7/2} \rightarrow ^{6}D_{I}$ (Gd³⁺) should be the dominant process in populating ⁶D₁ levels because of the strong absorption of Yb³⁺ under 980-nm excitation and the high concentration of Yb3+ in the samples. UV, violet, and blue UC emissions can be observed when transitions happen from the excited states ³P₂, ¹I₆, ¹D₂, ¹G₄ of Tm³⁺, and ⁶D_I, ⁶I_I, ⁶P_I levels of Gd³⁺.

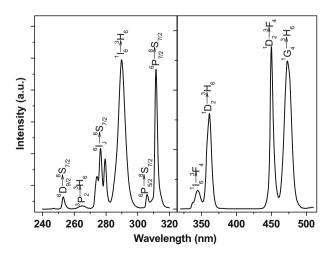


Fig. 3. Up-conversion emission spectrum of the $20\% Yb^{3+}$, $0.7\% Tm^{3+}$ co-doped NaGdF₄ under 980-nm excitation.

Fig. 3 presented an UC emission spectrum in the wavelength range of 240-510 nm of the 20%Yb³⁺, 0.7%Tm³⁺ co-doped NaGdF₄ sample, which was obtained with the excitation power about 600 mW of the 980-nm CW LD, and the spectrophotometer parameters Ex/Em slits were 1.0 nm, the high voltage of photomultiplier tube was 700 V, and the sensitivity was 0.2 nm, respectively. For clarity, the spectra were placed in the wavelength range of 240-320 and 320-510 nm. The emission that peaked at 253 nm was assigned to the transition $^6D_{9/2} \rightarrow {}^8S_{7/2}$ of Gd³+. The emission that centered at 264.8 nm came from the transition ${}^{3}P_{2} \rightarrow {}^{3}H_{6}$ of Tm³⁺. Emissions in the wavelength range of 270-282 nm (two peaks centering at 276.2 and 279.2 nm) came from the ${}^{6}I_{I} \rightarrow {}^{8}S_{7/2}$ transitions of Gd3+. The emission centered at 289.8 nm was assigned to the ${}^{1}I_{6} \rightarrow {}^{3}H_{6}$ transition of Tm³⁺. And, emissions peaked at 306 and 311.6 nm originated from the ${}^6P_{5/2} \rightarrow {}^8S_{7/2}$ and the $^6\mathrm{P}_{7/2} \rightarrow {}^8\mathrm{S}_{7/2}$ transitions of Gd³⁺, respectively. In the wavelength of 320-510 nm, all emissions were UC emissions of Tm³⁺. Emission that peaked at 344.6 nm came from the ${}^{1}I_{6} \rightarrow {}^{3}F_{4}$ transition. Emission those centered at 361.4 and 450 nm were ${}^{1}D_{2} \rightarrow {}^{3}H_{6}$ and $^1D_2 \to {}^3F_4$ transitions, respectively. And emission peaked at 472.8 nm originated from the $^1G_4 \to {}^3H_6$ transition.

To understand the above UC processes well, we investigated the excitation power dependence of UC fluorescence intensity of the samples. For an unsaturated UC process, the number of photons that is needed to populating the upper emitting state can be obtained by the following relation: $I_f \propto P^n$, where I_f is the fluorescence intensity, *P* is the pumping power of the excitation source, and *n* is the number of pumping light photons required [20]. Fig. 4 shows the typical double-logarithmic plots of I_f versus P of the 20%Yb³⁺, 0.7%Tm³⁺ co-doped NaGdF₄ sample. The fluorescence intensity for each spectral peak was represented by the integrated area between the corresponding spectral profile and the baseline. The nvalue was obtained from the slope of the linear fit. As illustrated of UC fluorescence intensity of Gd³⁺ dependence on the excitation power in Fig. 4a, n values obtained for 276.2, 279.2, 306, and 311.6 nm emissions were all around 5, indicating five-photon processes. For the emission peaked at 253 nm, the n value was 5.98 ± 0.29 , indicating that populating the $^6D_{9/2}$ level needed six 980-nm photons. Fig. 4b is the corresponding n values of Tm^{3+} . For 264.8 nm emission, the *n* value was 6.24 ± 0.45 , which meant that the UC emission was a six-photon process. For the emission of 289.8 and 344.6 nm, n values were 4.95 ± 0.15 and 4.83 ± 0.15 , which were five-photo processes. For the emission of 361.4 and 450 nm, *n* values were 4.03 ± 0.15 and 4.13 ± 0.11 , which were four-photon processes. For 472.8 nm emission, n value was 3.03 ± 0.10 , which indicated that populating the ${}^{1}G_{4}$ level needed

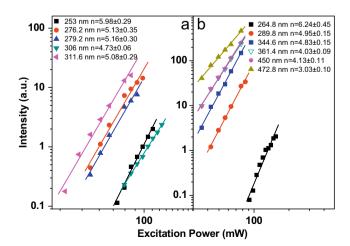


Fig. 4. Excitation power dependence of Gd^{3+} (a) and Tm^{3+} (b) upconversion fluorescence of the $20\%Yb^{3+}$, $0.7\%Tm^{3+}$ co-doped NaGdF₄.

three 980-nm photons. The results suggested that the UC emissions were three-, four-, five-, or six-photon processes.

For comparison, the UC emission spectra of the two samples were shown in Fig. 5. The red line is the UC emission spectrum of the 20%Yb³⁺, 0.7%Tm³⁺ co-doped NaGdF₄ sample, and the black line is the spectrum of the 20%Yb³⁺, 0.7%Tm³⁺ co-doped GdF₃ sample, which were both recorded under the same excitation conditions. The spectra were normalized to ${}^{1}G_{4} \rightarrow {}^{3}H_{6}$ of Tm^{3+} of each own. For the UC emissions in the wavelength range of 240-320 nm, $^6D_{9/2} \rightarrow ^8S_{7/2}$ and $^6I_J \rightarrow ^8S_{7/2}$ emissions (Gd³+) of 20%Yb³+, 0.7%Tm³+ co-doped NaGdF₄ sample were stronger than those of 20%Yb³+, 0.7%Tm³+ co-doped GdF₃ sample. On the contrary, $^6P_{5/2} \rightarrow ^8S_{7/2}$ and $^6P_{7/2} \rightarrow ^8S_{7/2}$ transitions (Gd³+) of 20%Yb³+, 0.7077 3+ $0.7\%\text{Tm}^{3+}$ co-doped NaGdF₄ sample were weaker than those of $20\%\text{Yb}^{3+}$, $0.7\%\text{Tm}^{3+}$ co-doped GdF₃ sample. In a word, for Gd³⁺, the 20%Yb³⁺, 0.7%Tm³⁺ co-doped NaGdF₄ sample trended to shorter wavelength UC emissions, while the 20%Yb3+, 0.7%Tm3+ co-doped GdF₃ sample inclined to longer wavelength UC emissions, and for 3P_2 , $^1I_6 \rightarrow ^3H_6$ transitions of Tm^{3+} , the emissions of the $20\%Yb^{3+}$, $0.7\%Tm^{3+}$ co-doped NaGdF₄ sample were stronger than those of the 20%Yb³⁺, 0.7%Tm³⁺ co-doped GdF₃ sample. In addition those, the branch ratio of ${}^{1}I_{6} \rightarrow {}^{3}H_{6}$ to ${}^{1}I_{6} \rightarrow {}^{3}F_{4}$ in the 20%Yb³⁺, 0.7%Tm³⁺ co-doped NaGdF₄ sample was larger than that of the 20%Yb³⁺, 0.7%Tm³⁺ co-doped GdF₃ sample, and the branch ratio of ${}^{1}D_{2} \rightarrow {}^{3}H_{6}$ to ${}^{1}D_{2} \rightarrow {}^{3}F_{4}$ in the 20%Yb³⁺, 0.7%Tm³⁺ co-doped NaGdF₄ sample was smaller than that of the 20%Yb³⁺, 0.7%Tm³⁺ codoped GdF₃ sample. At the same time, the emission peak positions of Tm³⁺ were different in the two samples. The emissions of the 20%Yb³⁺, 0.7%Tm³⁺ co-doped NaGdF₄ sample had slightly blue shift contrast to those of the 20%Yb³⁺, 0.7%Tm³⁺ co-doped GdF₃ sample. For ${}^{1}G_{4} \rightarrow {}^{3}H_{6}$ transitions of the two samples, they had different spectrum profiles. The 20%Yb³⁺, 0.7%Tm³⁺ co-doped GdF₃ sample had a weak shoulder in the short wavelength emission side, which could be clearly seen in Fig. 6. All these differences might have relations with the phase and structure of the samples, and the theoretical analysis was under intensively studied.

Fig. 6 shows the UC emissions of the two samples as functions of the excitation power. Fig. 6a and b are the spectra of the $20\%Yb^{3+}$, $0.7\%Tm^{3+}$ co-doped NaGdF₄ sample, and Fig. 6c and d are the spectra of the $20\%Yb^{3+}$, $0.7\%Tm^{3+}$ co-doped GdF₃ sample, where the excitation power increased from 50 to 700 mW from the bottom up in all the subfigures. One can easily learn that all UC emissions of the two samples became stronger with the excitation power increasing. Just as analyzed in the context, Gd³⁺ and

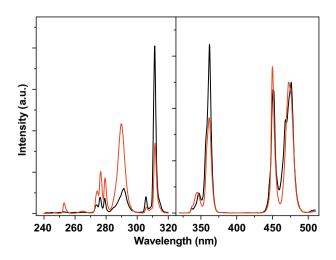


Fig. 5. Up-conversion emission spectra of the $20\%Yh^{3+}$, $0.7\%Tm^{3+}$ co-doped NaGdF₄ (red line), and GdF₃ (black line). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

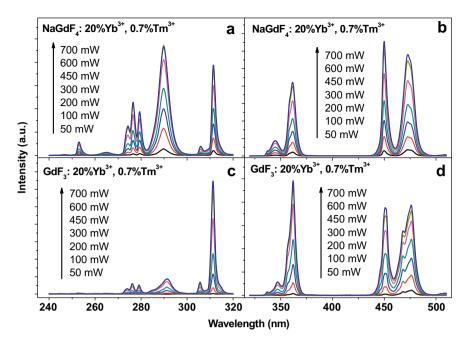


Fig. 6. Up-conversion emission spectra of the 20%Yb3*, 0.7%Tm3* co-doped NaGdF4 (a and b), and GdF3 (c and d) as functions of excitation power.

Tm³⁺ present different UC emissions in the two samples, and the figure gave further proofs of the spectra variation trends those analyzed above, too.

4. Conclusions

In conclusion, through an easy co-precipitation method and an argon atmosphere annealing procedure, the two 20%Yb3+, 0.7%Tm³⁺ co-doped GdF₃ and NaGdF₄ samples were synthesized. XRD analysis indicated that the 20%Yb³⁺, 0.7%Tm³⁺ co-doped GdF₃ sample was orthorhombic phase, and the 20%Yb³⁺, 0.7%Tm³⁺ co-doped NaGdF₄ sample was hexagonal phase. The UC emission spectra in the wavelength range of 240-510 nm were recorded with a 980-nm CW LD as the excitation source. The analysis of UC emissions indicated that Yb3+ acted as sensitizer ions in the emissions of Tm³⁺, and both Yb³⁺ and Tm³⁺ acted as sensitizer ions in the emissions of Gd³⁺. The experimental results suggested that the UC emissions of Gd³⁺ and Tm³⁺ were three-, four-, five-, or six-photon processes, and the two ions exhibited different UC emission properties in the two samples.

Acknowledgements

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