



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

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ABSTRACT

The Yb³⁺/Tm³⁺ co-doped GdF₃ and NaGdF₄ samples were synthesized through a combination method of a co-precipitation and an argon atmosphere annealing procedures. X-ray diffraction analysis indicated that the Yb³⁺/Tm³⁺ co-doped GdF₃ sample crystallized well and was orthorhombic phase, and the Yb³⁺/Tm³⁺ co-doped NaGdF₄ 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, Yb³⁺ transferred energies to Tm³⁺ resulting in their ultraviolet, violet, and blue up-conversion emissions. And, Tm³⁺ simultaneously transferred energies to Gd³⁺, which finally resulted in ultraviolet up-conversion emissions of Gd³⁺. 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 Gd³⁺ and Tm³⁺ in the Yb³⁺/Tm³⁺ co-doped GdF₃ and NaGdF₄ 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 near-infrared (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} (~32,000 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 ⁶I₁ and ⁶P₁ 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 ⁶D₁ levels to the ⁸S_{7/2} level emissions [12]. Subsequently, Chen et al. reported the near vacuum UV (VUV) UC emissions of Gd³⁺ under a 974-nm LD excitation [13]. To the best of our knowledge, there were no UC emission comparisons of Gd³⁺ or Tm³⁺ based on the NaGdF₄ and GdF₃ 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%Yb³⁺, 0.7%Tm³⁺ co-doped GdF₃ sample was synthesized according to the following procedure. Firstly, 7.93 mmol Gd₂O₃, 2 mmol Yb₂O₃, and 0.07 mmol Tm₂O₃, were dissolved in the dilute hydrochloric acid (HCl) at elevated temperature to form clear

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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} → ⁸S_{7/2} of Gd³⁺. The emission that centered at 264.8 nm came from the transition ³P₂ → ³H₆ of Tm³⁺. Emissions in the wavelength range of 270–282 nm (two peaks centering at 276.2 and 279.2 nm) came from the ⁶I_{7/2} → ⁸S_{7/2} transitions of Gd³⁺. The emission centered at 289.8 nm was assigned to the ¹I₆ → ³H₆ transition of Tm³⁺. And, emissions peaked at 306 and 311.6 nm originated from the ⁶P_{5/2} → ⁸S_{7/2} and the ⁶P_{7/2} → ⁸S_{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 ¹I₆ → ³F₄ transition. Emission those centered at 361.4 and 450 nm were ¹D₂ → ³H₆ and ¹D₂ → ³F₄ transitions, respectively. And emission peaked at 472.8 nm originated from the ¹G₄ → ³H₆ 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 n value 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 Tm³⁺. 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-photon 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 ¹G₄ level needed

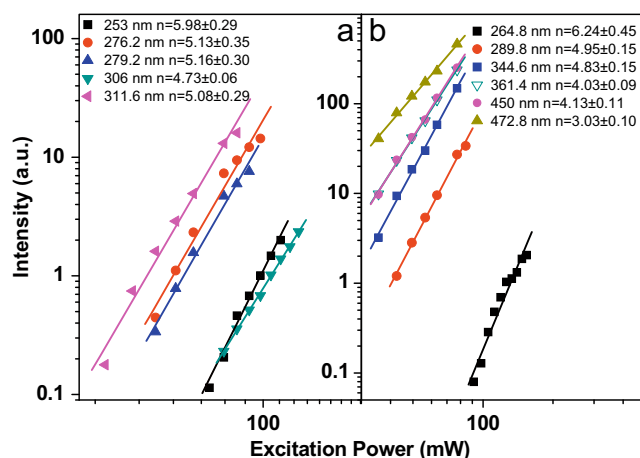


Fig. 4. Excitation power dependence of Gd³⁺ (a) and Tm³⁺ (b) upconversion fluorescence of the 20%Yb³⁺, 0.7%Tm³⁺ co-doped NaGdF₄.

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 ¹G₄ → ³H₆ of Tm³⁺ of each own. For the UC emissions in the wavelength range of 240–320 nm, ⁶D_{9/2} → ⁸S_{7/2} and ⁶I_{7/2} → 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} → ⁸S_{7/2} and ⁶P_{7/2} → ⁸S_{7/2} transitions (Gd³⁺) of 20%Yb³⁺, 0.7%Tm³⁺ co-doped NaGdF₄ sample were weaker than those of 20%Yb³⁺, 0.7%Tm³⁺ 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 ³P₂, ¹I₆ → ³H₆ transitions of Tm³⁺, the emissions of the 20%Yb³⁺, 0.7%Tm³⁺ 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 ¹I₆ → ³H₆ to ¹I₆ → ³F₄ 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 ¹D₂ → ³H₆ to ¹D₂ → ³F₄ in the 20%Yb³⁺, 0.7%Tm³⁺ co-doped NaGdF₄ sample was smaller than that of the 20%Yb³⁺, 0.7%Tm³⁺ co-doped 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 ¹G₄ → ³H₆ 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%Yb³⁺, 0.7%Tm³⁺ co-doped NaGdF₄ sample, and Fig. 6c and d are the spectra of the 20%Yb³⁺, 0.7%Tm³⁺ 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

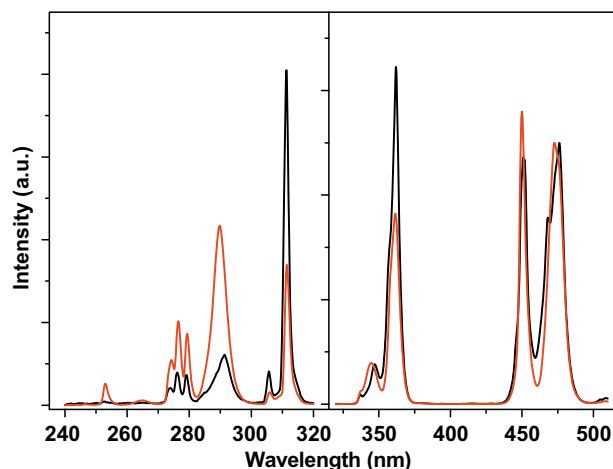


Fig. 5. Up-conversion emission spectra of the 20%Yb³⁺, 0.7%Tm³⁺ co-doped NaGdF₄ (red line), and GdF₃ (black line). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

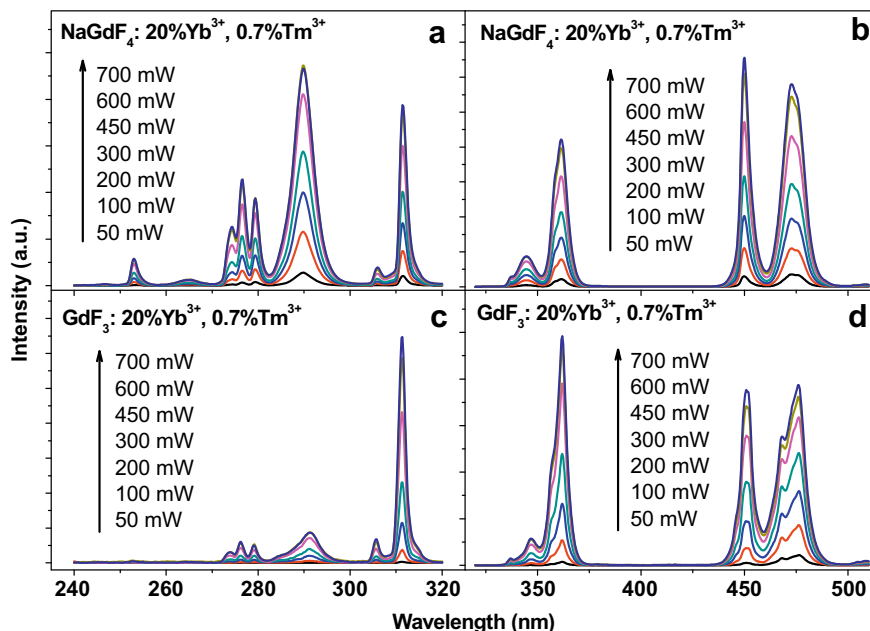


Fig. 6. Up-conversion emission spectra of the 20%Yb³⁺, 0.7%Tm³⁺ co-doped NaGdF₄ (a and b), and GdF₃ (c and d) as functions of excitation power.

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.

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