Ultraviolet upconversion fluorescence from ^6D_J of Gd^{3+} induced by 980 nm excitation

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Ultraviolet upconversion emissions of 246.2 and 252.8 nm from ^6D_J levels of Gd^{3+} ions were observed in GdF_3: 10% Yb^{3+}, 0.7% Tm^{3+} nanocrystals under 980 nm excitation from a laser diode. The ^6D_J levels of Gd^{3+} ions can be efficiently populated by energy transfer processes of Yb→Tm→Gd and Yb→Gd. A six-photon upconversion process was confirmed by the dependence of 252.8 nm emission intensity on the pumping power. The upconversion mechanism in the six-photon process was discussed based on excited state absorption of Gd^{3+} ions, cross relaxation energy transfer between two excited Gd^{3+} ions, and energy transfer between Gd^{3+} and Yb^{3+} or Tm^{3+} ions. © 2008 Optical Society of America

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Rare earth ions have ample electronic state levels and have been widely used in frequency upconversion (UC) materials. Tm, Er, Yb, Ho, Pr, etc., have been studied extensively as activators in UC materials for their monochromatic fluorescence in visible and ultraviolet (UV) optical regions. Trivalent gadolinium ions (Gd^{3+}) have a $4f^7$ electronic configuration, and the energy gap between the ground state $^8S_{7/2}$ and the first excited state $^6P_{7/2}$ is 32,000 cm^{-1}. Although its spectral properties have been theoretically and experimentally studied [1–4], UC emissions based on Gd^{3+} ions have rarely been reported owing to the large energy gap. Two exceptive observations came from the experiments reported by Gharavi and McPherson [5] and Cao *et al.* [6], respectively. The former observed 281 and 313 nm UC emissions of Gd^{3+} ions by using Er^{3+} ions as sensitizers and green lasers (546 and 522 nm) as pump lights, and the latter obtained the shortest wavelength (273 nm) on record of UC emissions by using Yb^{3+} and Tm^{3+} as sensitizers and a 980 nm diode laser as pump light.

In this Letter, we presented an observation of ~246.2 and 252.8 nm UC emissions from Gd^{3+} ions in Tm^{3+}–Yb^{3+} codoped GdF_3 nanocrystals under 980 nm excitation. To the best of our knowledge, 246.2 nm is an all-time short wavelength record of UC emissions under an IR excitation, and especially, these UV UC emissions upconverted from the IR region are attributed to a six-photon process. In the GdF_3: Tm^{3+}–Yb^{3+} system, both Yb^{3+} and Tm^{3+} served as sensitizers in exciting Gd^{3+} ions, while Tm^{3+} ions acted concurrently as activators. Under 980 nm excitation, Yb^{3+} ions continuously absorbed the photons and transferred energies to Tm^{3+} ions. Further energy transfer (ET) occurred from the Tm^{3+} ions in the high excited state $^3P_2$ to the Gd^{3+} ions in the ground state $^8S_{7/2}$ and resulted in the populations of the ^6I_J and ^6P_J levels of these Gd^{3+} ions. Subsequently, the excited Gd^{3+} ions absorbed energy further and populated at higher energy levels of ^6D_J.

GdF_3: 10% Yb^{3+}, 0.7% Tm^{3+} nanocrystals were synthesized through a coprecipitation method with analytical reagents and annealed under an Ar atmosphere at 700°C for 1 h. Powder x-ray-diffraction analysis revealed that the sample was orthorhombic phase. Morphological analysis with field-emission scanning electron microscopy showed that the annealed sample was agglomerate particles. Under 980 nm excitation, the sample emitted UV light, and the UC emission spectra were recorded with a fluorescence spectrophotometer (Hitachi F-4500). The temporal evolution of UV emissions was investigated at the onset of a 980 nm pulsed laser from an optical parametric oscillator (OPO) pumped by a 10 ns pulsed Nd:YAG laser. The signal was recorded by using a monochromator and an oscillograph. All measurements were performed at room temperature.

At 980 nm excitation of ~400 mW, the annealed sample emitted intense UV UC fluorescence. Figure 1(a) shows the UC emission spectrum in the range of 240–270 nm. The emissions that peaked at 246.2

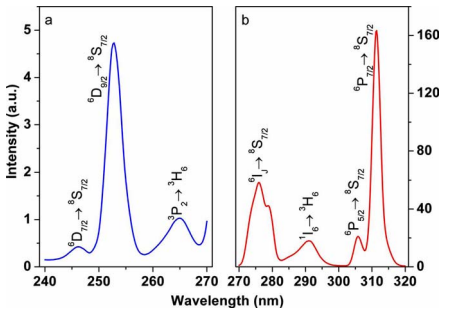

Fig. 1. (Color online) UC emission spectra of GdF_3: 10% Yb^{3+}, 0.7% Tm^{3+} under 980 nm excitation.

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and 252.8 nm were assigned to the transitions from ${}^6D_{J(J=1/2,3/2,5/2,7/2)}$ and ${}^6D_{9/2}$ to ${}^8S_{7/2}$ of Gd^{3+} ions, respectively; 246.2 nm is a new record of IR-to-UV UC fluorescence. The emission that centered at 265.0 nm came from the transition ${}^3P_2 \rightarrow {}^3H_6$ of Tm^{3+} ions. Figure 1(b) shows the UC emission spectrum in the range of 270–320 nm. Emissions in the range of 270–282 nm (two peaks centered at 276.8 and 279.0 nm) came from the ${}^6I_J \rightarrow {}^8S_{7/2}$ transitions of Gd^{3+} [6]. The emission peak at 291.4 nm was assigned to the ${}^1I_6 \rightarrow {}^3H_6$ transition of Tm^{3+}, and 306.0 and 311.6 nm emissions originated from the ${}^6P_{5/2} \rightarrow {}^8S_{7/2}$ and the ${}^6P_{7/2} \rightarrow {}^8S_{7/2}$ transitions of Gd^{3+}, respectively [6].

Figure 2 describes schematically possible upconverted processes in energy level diagrams [7,8] of Gd^{3+}, Yb^{3+}, and Tm^{3+}. In a Tm^{3+}–Yb^{3+}–Gd^{3+} coexisting system, as analyzed in [6], Yb^{3+} ions successively transfer energy to Tm^{3+} to populate the ${}^3H_5$, ${}^3F_3$ (${}^3F_2$), and ${}^1G_4$ levels in turn [9]. The ${}^1D_2$ state is populated through the cross relaxation ${}^3F_3 \rightarrow {}^3H_6$: ${}^3F_3 \rightarrow {}^1D_2$ (Tm^{3+}) [10,11]. 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+}). Then, some of the Tm^{3+} ions in the ${}^3P_2$ state make the radiative transition of ${}^3P_2 \rightarrow {}^3H_6$, and some of them relax rapidly to the ${}^1I_6$ level, resulting in ${}^1I_6 \rightarrow {}^3H_6$, ${}^3F_4$ transitions. Gd^{3+} ions in the ground state cannot absorb 980 nm photons directly because of the large energy gap between the ground state ${}^8S_{7/2}$ and the first excited state ${}^6P_J$. However, the excited states ${}^6I_J$ of Gd^{3+} can be populated through the ET ${}^3P_2 \rightarrow {}^3H_6$ (Tm^{3+}): ${}^8S_{7/2} \rightarrow {}^6I_J$ (Gd^{3+}). At room temperature, the nonradiative relaxation probability of ${}^6I_J \rightarrow {}^6P_J$ is larger than the radiative transition probability of ${}^6I_{7/2} \rightarrow {}^8S_{7/2}$ [12], which results in populating ${}^6P_{5/2}$ and ${}^6P_{7/2}$ levels efficiently. Furthermore, the ${}^6D_J$ levels of Gd^{3+} ions can be populated by another transition process from the ${}^6I_J$ or ${}^6P_J$ state. This population process requires the energy ranged in 6500–8500 cm^{-1} for the transition of ${}^6P_J \rightarrow {}^6D_J$ (Gd^{3+}) or 3700–4300 cm^{-1} for the transition of ${}^6I_J \rightarrow {}^6D_J$ (Gd^{3+}). Three mechanisms should be considered in populating ${}^6D_J$ levels, *viz.*, excited state absorption (ESA), cross relaxation resonant energy transfer (CRET), and ET. For the ESA mechanism of ${}^6P_J + h\nu \Rightarrow {}^6D_J$, the 980 nm (~10200 cm^{-1}) photon offers excess energy and will release a high energy phonon (~1700–3700 cm^{-1}) or several low energy phonons. Therefore, it will occur with a very low probability. For the CRET of ${}^6I_J \rightarrow {}^6P_J$ (Tm^{3+}): ${}^6I_J \rightarrow {}^6D_J$ (Tm^{3+}), as shown in Fig. 2, the energy matching is good, however, this process not only requires sufficient ${}^6I_J$ population but also should show a ten-photon UC process. The excitation power dependence of ${}^6D_J$ fluorescence intensity did not support such a ten-photon UC process as discussed below. Therefore, the CRET cannot be the main mechanism in populating the ${}^6D_J$ state. For the ET mechanism, many transition processes, radiative or nonradiative, can offer approximate energy for the transition of ${}^6P_J \rightarrow {}^6D_J$ or ${}^6I_J \rightarrow {}^6D_J$, such as the transition of ${}^2F_{5/2} \rightarrow {}^2F_{7/2}$ (~10000 cm^{-1}), ${}^3P_{0,1} \rightarrow {}^1D_2$ (~8800, ~9000 cm^{-1}), ${}^3F_{2,3} \rightarrow {}^3H_5$ (~6400, ~6900 cm^{-1}), ${}^1G_4 \rightarrow {}^3H_4$, ${}^3F_{2,3}$ (~9000, 6400, 7000 cm^{-1}), and ${}^3H_4 \rightarrow {}^3H_5$ (~4300 cm^{-1}), owing to their appropriate energy matching. Generally speaking, the ET of ${}^2F_{5/2} \rightarrow {}^2F_{7/2}$ (Yb^{3+}): ${}^6P_{7/2} \rightarrow {}^6D_J$ (Gd^{3+}) should be dominant in populating ${}^6D_J$ levels not only because of the high concentration of Yb^{3+} ions in the sample but also because of the strong IR absorption of Yb^{3+} ions. However, the large mismatch ($\geqslant$1700 cm^{-1}) of energy makes it occur with a low probability, which results in a low ${}^6D_J$ population and weak emissions from ${}^6D_J$ levels.

The temporal evolution of Gd^{3+} fluorescence in the nanocrystal was studied and the decay curve for the representative emission (311.6 nm) from ${}^6P_{7/2}$ was recorded as shown in Fig. 3. This decay curve can be fitted well into an exponential function as $I = I_0 \exp(-t/\tau)$. According to the best-fitted result in Fig. 3, τ ($\approx$950 μs) is the lifetime of ${}^6P_{7/2}$ levels. The ${}^6P_{7/2}$ level has a long enough lifetime to accept the migrated energy from Yb^{3+} or Tm^{3+} and populate the upper ${}^6D_J$ levels.

To understand the UC processes well, we investigated the excitation power dependence of UC fluorescence intensity. For an unsaturated UC process, the number of photons that is necessary to populate 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 IR laser, and n is the number of laser photons required [13]. Figure 4 shows the typical double-logarithmic plots of I_f versus P. The fluorescence intensity for each spectral peak was represented by the integrated area between

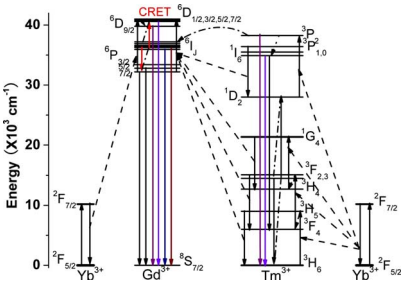

Fig. 2. (Color online) Energy level diagrams of Gd^{3+}, Yb^{3+}, and Tm^{3+} ions and possible upconverted processes.

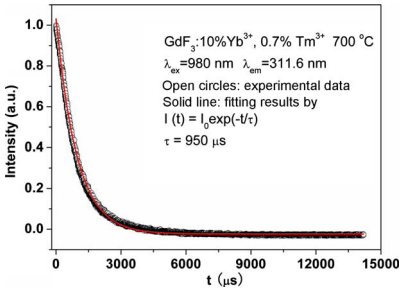

Fig. 3. (Color online) Decay curve of 311.6 nm UC emission of GdF_3: 10% Yb^{3+}, 0.7% Tm^{3+}.

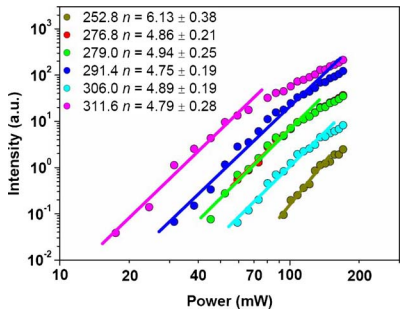

Fig. 4. (Color online) Excitation power dependence of UC fluorescence of GdF_3: 10% Yb^{3+}, 0.7% Tm^{3+}.

the corresponding spectral profile and the baseline. The n value was easily obtained from the slope of the linear fit. As illustrated in Fig. 4, n values obtained for 276.8, 279.0, 291.4, 306.0, and 311.6 nm emissions were all around 5, indicating five-photon processes. For the emission peaked at 252.8 nm, the n value was 6.13 ± 0.38, indicating that populating the $^6D_{9/2}$ level needed six 980 nm photons and was a six-photon UC process.

Figure 5 is the excitation power dependence of UC emission spectra of the sample. As we can see, when the excitation power increased from 100 to 450 mW, the 252.8 nm emission of Gd^{3+} ions appeared and gradually got stronger. At the same time, the 276.8 nm emission predominated over the 279.0 nm emission. In general, the populations on two nearby levels followed Boltzmann's distribution law, therefore the strange and interesting spectral profile should mean that more than one level of ^6I_J multiplets have been included in the 276.8 nm emission. The energy difference between 276.8 and 279.0 nm emissions is only $\sim 284\ cm^{-1}$. The thermal transition between ^6I_J multiplets should be the main reason in producing the interesting spectral profile. The inset

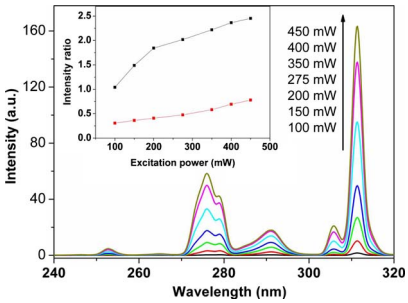

Fig. 5. (Color online) Excitation power dependence of UC emission spectra of GdF_3: 10% Yb^{3+}, 0.7% Tm^{3+}. The upper curve in the inset is the integrated intensity ratio of 276.8–279.0 nm emissions, and the lower curve is the integrated intensity ratio of all emissions from Gd^{3+} to those from the $^1I_6$ of Tm^{3+}.

in Fig. 5 shows the integrated emission intensity ratio of 276.8–279.0 nm (the upper curve). Clearly, the ratio becomes larger with the increase of excitation power because the temperature of the sample is increased with the increasing excitation power. The lower curve in the inset is the total integrated intensity of Gd^{3+} emissions to the total integrated intensity of Tm^{3+} emissions from $^1I_6$ ($^1I_6 \rightarrow {}^3H_6$, $^3F_4$). When the excitation power is 450 mW, the ratio reaches 0.78, which reveals that the ET from $^3P_2$ (Tm^{3+}) to ^6I_J (Gd^{3+}) is rather efficient and reduces the population on the $^1I_6$ level.

In conclusion, GdF_3: 10% Yb^{3+}, 0.7% Tm^{3+} nanocrystals were synthesized through a coprecipitation method. Under 980 nm excitation, the annealed nanocrystals emitted UV UC fluorescence. In addition to the UC emissions from the ^6I_J and ^6P_J levels of Gd^{3+} ions, 246.2 and 252.8 nm UC fluorescence were observed and assigned to the $^6D_J \rightarrow {}^8S_{7/2}$ transitions of Gd^{3+} ions. Power dependence experiments confirmed that the emissions from ^6D_J came from a six-photon process. The mechanism of the six-photon UC process was discussed based on ESA, CRET, and ET processes.

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