Ultraviolet upconversion emissions of Gd^{3+}

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Under 980 nm excitation, upconversion (UC) emissions in the UV range of 270–320 nm were observed in nanocrystals $Y_{0.795-x}Gd_xYb_{0.2}Tm_{0.005}F_3$ ($x=0$, 0.1, 0.2, 0.5, and 0.795), which were synthesized through a hydrothermal method. These UC emissions can be assigned to the transitions of ^6I_J, $^6P_J \rightarrow {}^8S_{7/2}$ (Gd^{3+}), and $^3P_0/^1I_6 \rightarrow {}^3H_6$ (Tm^{3+}). The energy transfer from Tm^{3+} to Gd^{3+} plays a crucial role in populating the excited states of Gd^{3+}. The shortest wavelength of upconverted emission converted from the infrared region was demonstrated here. © 2008 Optical Society of America

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In recent years, short-wavelength compact solid-state lasers in the spectral range of UV to green have attracted much attention because of their potential applications, such as optical data storage, color displays, IR sensors, environmental monitoring, and so on [1–3]. Frequency upconversion (UC) in optical generation is an important mechanism for achieving short-wavelength laser radiation, especially within rare-earth (RE) materials. With the benefits of intrinsic energy levels matching certain RE ions and the ample availability of laser diodes in the visible and IR range, some attractive predictions have already been made in developing short-wavelength compact solid-state lasers [3]. Though visible UC emissions have been extensively investigated in the past 40 years [3–6], efficient UV UC emissions induced by IR lights have rarely been reported except for some Tm^{3+}–Yb^{3+} codoped compounds [7–11].

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}. Such a spectral characteristic determines that Gd has a wide range of applications. For example, Gd_2SiO_5 [12], Gd_2O_3 [13,14] $LiGdF_4$ [15,16], $GdBO_3$ [17], and GdF_3 [18] were usually used as host materials or commercial phosphors.

Spectral properties of Gd^{3+}, in a free-state, crystalline environment, and glass have been theoretically and experimentally studied [19–21], especially under vacuum UV (VUV) excitations [21,22]. On the contrary, UC emissions of Gd^{3+} have rarely been reported until now, to the best of our knowledge; the only example can be found in [23], which reported that UC emissions of Gd^{3+} peaked at 281 and 313 nm. However, in their experiments, the researchers used Er^{3+} ions as sensitizers and green lasers (546 and 522 nm) as pump lights. By exciting the energy levels $^4S_{3/2}$ and $^2H_{11/2}$ of Er^{3+}, they carried out a cooperative energy transfer (ET) from Er^{3+} to Gd^{3+} and observed the UV UC emissions of Gd^{3+}.

In this Letter, we present an observation of IR-to-UV UC emissions from Gd^{3+} ions in Gd^{3+}–Yb^{3+}–Tm^{3+} coexisting nanocrystals and report the shortest wavelength (~273 nm) of frequency UC emission from the IR region. The nanocrystals were synthesized using a hydrothermal method. Both Yb^{3+} and Tm^{3+} ions acted as sensitizers in the luminescence of Gd^{3+}. With a 980 nm continuous wave laser diode as the excitation source, Yb^{3+} ions absorbed IR photons and transferred the energy to Tm^{3+} ions. Further ET occurred from Tm^{3+} to Gd^{3+} and resulted in the UV emissions of Gd^{3+}.

The starting materials were all analytical reagents. Series samples $Y_{0.795-x}Gd_xYb_{0.2}Tm_{0.005}F_3$ ($x=0$, 0.1, 0.2, 0.5, and 0.795) were synthesized according to the procedure described in [24]. After being annealed under an Ar atmosphere at 600°C for 1 h, the sample emitted bright blue and intense UV light under 980 nm excitation. To identify the crystallization phase, x-ray-diffraction (XRD) analysis was carried out with a powder diffractometer (Model Rigaku RU-200b), using Ni-filtered Cu$K\alpha$ radiation ($\lambda=1.5406$ Å). The size and the morphology were characterized by field-emission scanning-electron microscopy (FE-SEM) (Hitachi S-4800). UC emission spectra were recorded with a fluorescence spectrophotometer (Hitachi F-4500). All measurements were performed at room temperature.

Figure 1 shows XRD patterns of the annealed sample $Y_{0.595}Gd_{0.2}Yb_{0.2}Tm_{0.005}F_3$ and the standard data for YF_3, GdF_3, and YbF_3. All of these fluorides are orthorhombic phase with the same space group Pnma (62). So, whatever their proportions were in starting materials, the samples could crystallize well. The inset in Fig. 1 shows the FE-SEM image of the sample. It is clear that the samples were composed of aggregated particles with an average size of ~100 nm.

Under 980 nm excitation with a pump-power density of ~200 W/cm^2, the nanocrystal $Y_{0.595}Gd_{0.2}Yb_{0.2}Tm_{0.005}F_3$ emitted UV UC fluorescence, as shown in Fig. 2. Three emission peaks in the range of 270–281 nm came from the $^6I_J \rightarrow {}^8S_{7/2}$ transitions of Gd^{3+}. The emission that was centered

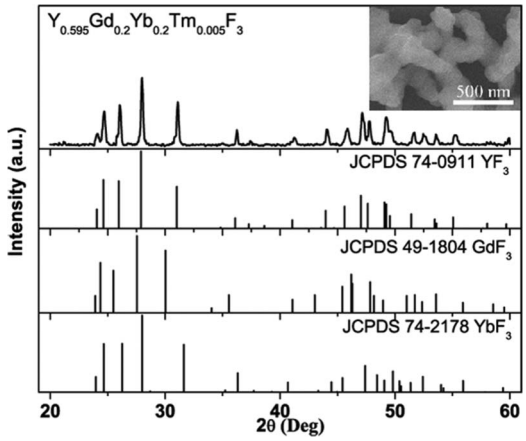

Fig. 1. XRD patterns of annealed sample $Y_{0.595}Gd_{0.2}Yb_{0.2}Tm_{0.005}F_3$, and standard data of YF_3, GdF_3, and YbF_3.

at 291 nm was assigned to the $^3P_0/^1I_6 \rightarrow {}^3H_6$ transition of Tm^{3+}. Emissions that peaked at 305 and 311 nm originated from the $^6P_{5/2} \rightarrow {}^8S_{7/2}$ and the $^6P_{7/2} \rightarrow {}^8S_{7/2}$ transitions of Gd^{3+}, respectively. The inset in Fig. 2 shows the pump-power dependences of the UC emissions. According to the relation $I_f \propto P^n$ [25], n values were 4.8 ± 0.2, 5.0 ± 0.2, and 4.9 ± 0.2 for 291, 305, and 311 nm emissions, respectively, indicating five-photon processes.

Figure 3 is the energy level diagram of Gd^{3+}, Yb^{3+}, and Tm^{3+} ions [26,27]. In a Tm^{3+}–Yb^{3+} codoped system, Yb^{3+} ions absorb the pumping photons of a 980 nm laser and successively transfer energy to Tm^{3+} ions to populate their $^3H_5$, $^3F_3$ ($^3F_2$), and $^1G_4$ levels [28]. Since the $^1D_2$ level cannot be directly populated by the ET $^2F_{5/2} \rightarrow {}^2F_{7/2}$ (Yb^{3+}):$^1G_4 \rightarrow {}^1D_2$ (Tm^{3+}) owing to the large energy mismatch ($\sim 3500\ cm^{-1}$) between them, the $^1D_2$ level may alternatively be populated through the cross-relaxation $^3F_3 \rightarrow {}^3H_6$:$^3F_3 \rightarrow {}^1D_2$ (Tm^{3+}) [29,30]. Then, the $^3P_{2,1}$ (Tm^{3+}) levels are populated by the ET $^2F_{5/2} \rightarrow {}^2F_{7/2}$ (Yb^{3+}):$^1D_2 \rightarrow {}^3P_{2,1}$ (Tm^{3+}) [10]. The $^3P_{2,1}$ levels nonradiatively decay to the $^3P_0$ and $^1I_6$ (Tm^{3+})

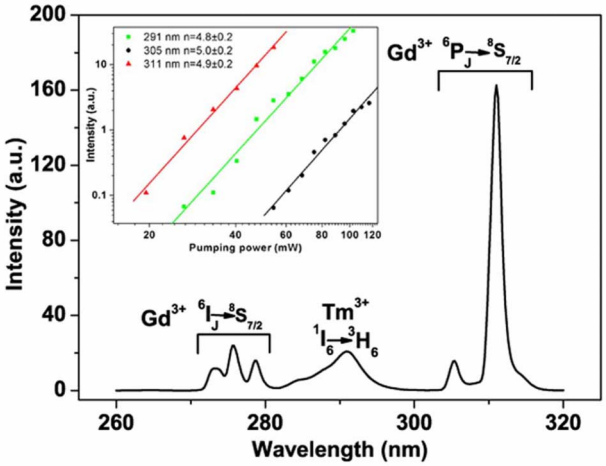

Fig. 2. (Color online) Upconversion emission spectrum of the sample $Y_{0.595}Gd_{0.2}Yb_{0.2}Tm_{0.005}F_3$. The inset is the pump-power dependence of the emissions.

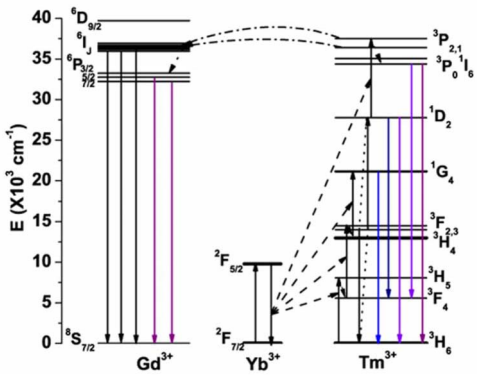

Fig. 3. (Color online) Schematic energy level diagrams of Gd^{3+}, Yb^{3+}, Tm^{3+}, and upconverted emission processes.

levels. Blue ($^1D_2 \rightarrow {}^3F_4$ and $^1G_4 \rightarrow {}^3H_6$) and UV emissions ($^3P_0/^1I_6 \rightarrow {}^3H_6$, $^3P_0/^1I_6 \rightarrow {}^3F_4$ and $^1D_2 \rightarrow {}^3H_6$) of Tm^{3+} can be observed. For the large energy gap between the ground state and the first excited state, the Gd^{3+} cannot absorb 980 nm photons directly. In a Tm^{3+}–Yb^{3+}–Gd^{3+} codoped system, the excited states ^6I_J of Gd^{3+} can be populated through the ET $^3P_{2,1} \rightarrow {}^3H_6$ (Tm^{3+}):$^8S_{7/2} \rightarrow {}^6I_J$ (Gd^{3+}). At room temperature, the probability of the nonradiative relaxation from the $^6I_{7/2}$ level to the $^6P_{5/2}$ level of Gd^{3+} is approximately 5 times larger than the probability of the radiative transition $^6I_{7/2} \rightarrow {}^8S_{7/2}$ in $LiYF_4$ [31]. So the nonradiative decay $^6I_J \rightarrow {}^6P_J$ results in $^6P_J \rightarrow {}^8S_{7/2}$ emissions. Then, UV emissions from Gd^{3+} ions were observed when the excited states ^6I_J and/or ^6P_J depopulated radiatively to the ground state. Based on the above analysis, we deduced that it is of central importance to populate the $^3P_{2,1}$ levels efficiently for obtaining intense UV UC emissions of Gd^{3+} in the Yb^{3+}–Tm^{3+}–Gd^{3+} codoped system.

To prove the ET from Tm^{3+} to Gd^{3+} further, we compared the emission spectrum of the sample $Y_{0.595}Gd_{0.2}Yb_{0.2}Tm_{0.005}F_3$ to that of $Y_{0.795}Yb_{0.2}Tm_{0.005}F_3$, as shown in Fig. 4. The spectra were all recorded under the same conditions (emission and excitation slits are 2.5 nm, high voltage of the photomultiplier tube is 700 V, and the excitation

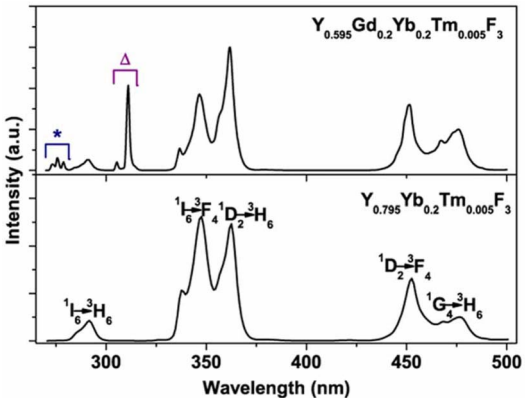

Fig. 4. (Color online) Upconversion emission spectra of $Y_{0.595}Gd_{0.2}Yb_{0.2}Tm_{0.005}F_3$ and $Y_{0.795}Yb_{0.2}Tm_{0.005}F_3$ recorded under the same conditions. The peaks marked by * and △ are emissions of Gd^{3+}.

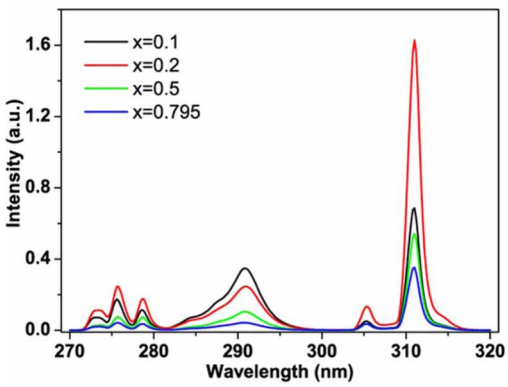

Fig. 5. (Color online) Upconversion emission spectra of annealed samples $Y_{0.795-x}Gd_xYb_{0.2}Tm_{0.005}F_3$ ($x=0.1$, 0.2, 0.5, and 0.795).

power density is about 200 W/cm^2). The peaks marked by an asterisk (*) and a triangle (△) are emissions of Gd^{3+}. As analyzed in this context, the populations of the excited states ^6I_J and ^6P_J of Gd^{3+} should be induced by the ET from the excited Tm^{3+}. The reduced intensity of the transitions $^3P_0/^1I_6 \rightarrow {}^3H_6$, $^3F_4$ also offered evidence of the ET process.

To obtain strong UV UC emissions of Gd^{3+}, we optimized host materials by adjusting their components. However, $Tm^{3+}-Yb^{3+}$ codoped GdF_3 did not show intense emissions of Gd^{3+} though the characteristic emissions of Gd^{3+} were observed in our experiments. A previous investigation indicates that YF_3 is a good host material for IR-to-visible UC emissions [32]. Figure 5 shows UC emission spectra of samples $Y_{0.795-x}Gd_xYb_{0.2}Tm_{0.005}F_3$ ($x=0.1$, 0.2, 0.5, and 0.795), which were all recorded under the same conditions. With the increase of Gd^{3+} concentration, emissions from Gd^{3+} first increased and then decreased, while the emission $^3P_0/^1I_6 \rightarrow {}^3H_6$ of Tm^{3+} always decreased, which also creates more evidence of the ET from Tm^{3+} to Gd^{3+}. Meanwhile, the variation of the fluorescence intensity in the spectra implies that there could be concentration quenching occurring between Gd^{3+} ions.

In conclusion, $Y_{0.795-x}Gd_xYb_{0.2}Tm_{0.005}F_3$ ($x=0$, 0.1, 0.2, 0.5, and 0.795) nanocrystals were synthesized through a hydrothermal method. After annealing, the nanocrystals emitted intense UV and blue light under 980 nm excitation. The experimental data indicate that, in the complex excitation and frequency UC processes, the ETs in succession from Yb^{3+} to Tm^{3+} and from Tm^{3+} to Gd^{3+} played key roles. Intense UV UC emissions of the Gd^{3+}-doped nanocrystals suggest a possible candidate material for building UV compact solid-state lasers or fiber lasers.

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