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Improved Ultraviolet Upconversion Emissions of Ho^{3+} in Hexagonal $NaYF_4$ Microcrystals Under 980 nm Excitation

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Under 980 nm excitation, enhanced ultraviolet (UV) upconversion (UC) emissions at 242.4 nm, 276.1 nm, 289.7 nm, 296.4 nm, 303.6 nm, 357.7 nm and 387.8 nm of Ho^{3+} ions were observed in β-$NaYF_4$:20%Yb^{3+}, 1.5%Ho^{3+} microcrystals (MC) which were synthesized through a hydrothermal method. The results indicated that these UV emissions came from five- and four-photon UC processes. Dynamical analysis on Ho^{3+} excited states suggests that, for excited Ho^{3+} ions, the higher the energy level is, the shorter the lifetime is.

Keywords: Ultraviolet, Upconversion, Ho^{3+}.

1. INTRODUCTION

Short-wavelength solid-state lasers in the UV to green spectral range have attracted much attention in recent years because of a wide range of applications, including biomedicine, 3-D displays, and compact solid-state lasers.[1–7] UC pumping by means of intrinsic energy level matching of certain rare earth ions plays a significant role in achieving short wavelength laser radiation because of the ample availability of pump diode lasers in the IR range. Especially, the study around IR-to-UV UC compact solid-state lasers is extremely attractive not only because IR laser diodes are compact, power-rich, and inexpensive, but also because UV solid-state lasers have unique potential applications in electronic industry. On the other hand, the UV-generated UC emissions can also be used in the field of biomedicine, in which UV emissions contribute towards the production of singlet oxygen for photodynamic therapies.[8,9] Consequently, it has been a great challenge for researchers today to synthesize high-efficiency UV UC luminescence materials.

Yb^{3+} ions have a long excited-state lifetime. They were often chosen as an IR sensitizer in codoped systems[10–12] In recent years, green visible emissions by infrared pump in Yb^{3+}–Ho^{3+} codoped UC luminescence materials have been very well explained as energy transfer (ET) from excited Yb^{3+} ions by stepwise UC mechanisms.[13–16] However, there is little work on UV optical properties of Ho^{3+} ions in β-phase $NaYF_4$. It is well-established that β-$NaYF_4$ is one of the most efficient UC host materials under 980 nm NIR excitation due to its low phonon modes (300–400 cm^{-1}). Multi-phonon relaxation is reduced, increasing the probability of radiative transitions.[17–19] The study to obtain UV luminescence of Ho^{3+} in efficient matrix is still a challenge for the development of short-wavelength solid-state lasers.[19]

In this letter, we presented an observation of UV UC emissions from Ho^{3+} ions in Yb^{3+}–Ho^{3+} codoped β-$NaYF_4$ microcrystals (MCs). Upon excitation with NIR radiation of 980 nm, 242.4 nm, 276.1 nm, 289.7 nm, 296.4 nm, 303.6 nm, 357.7 nm and 387.8 nm UC emissions of Ho^{3+} were recorded. In the MCs, Yb^{3+} ions, served as sensitizers, absorbed NIR photons and transferred the energy to Ho^{3+} ions consecutively to populate their high-energy states. The high-energy state $^3F_4/^5D_4$ of Ho^{3+} ions were populated by a five-photon UC process.

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2. EXPERIMENTAL DETAILS

Analytical grade $Y(NO_3)_3 \cdot 6H_2O$, $Ho(NO_3)_3 \cdot 6H_2O$, $Yb(NO_3)_3 \cdot 6H_2O$, NaF, ethanol, and EDTA were obtained from Beijing Chemical Reagents, China. Deionized water was used throughout. All other chemical reagents were of analytical reagent grade. In a typical synthesis, 1 mL of 0.5 M $Ln(NO_3)_3$ aqueous solution and 0.5 mmol EDTA were dispensed into 20 mL of deionized water and magnetically stirred for 1 h, forming a chelated Ln-EDTA complex. Then 16 mL of 0.5 M NaF aqueous solution was added to the solution. After vigorous stirring for 1 h, the mixture was transferred into a 50-mL Teflon-lined stainless steel autoclave. The autoclave was sealed and maintained in an oven at 160 °C for 15 h, and then cooled down slowly to room temperature. Subsequently, the suspension was centrifuged at 8000 rpm for 10 min. The resultant product was then washed thoroughly and dried in vacuum at 80 °C.

3. RESULTS AND DISCUSSION

The crystal structure was analyzed by a Rigaku RU-200b X-ray powder diffractometer (XRD) using a nickel-filtered Cu-K*a* radiation ($\lambda = 1.4518$ Å). The size and morphology were investigated by scanning electron microscope (SEM, KYKY 1000B). A power-adjustable laser diode (980 nm, 0 to 2 W) with a lens making the beam parallel was employed as the UC pump source. The UC luminescence spectra were recorded with a Hitachi F-4500 fluorescence spectrophotometer at room temperature. A 10-ns Raman laser running at 953.6 nm was used as the pulsed excitation source for temporal investigations. Figure 1 shows the XRD pattern of the MCs. All the diffraction peaks can be indexed to the pure hexagonal $NaYF_4$ (JCPDS 16-0334). No other impurity peaks were detected. The corresponding SEM image (Fig. 1) shows that the $NaYF_4$:Yb^{3+}/Ho^{3+} MCs are hexagonal pillars.

Figures 2 and 3 display the UC emissions of $NaYF_4$: 20%Yb^{3+}, 1.5%Ho^{3+} under 980 nm excitation. UV and visible UC emissions of Ho^{3+} ions can be seen clearly.

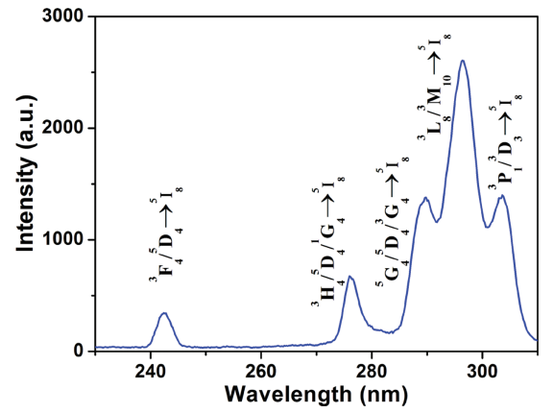

Figure 2. UV UC spectrum of $NaYF_4$:20%Yb^{3+}, 1.5%Ho^{3+} MCs under 980 nm excitation.

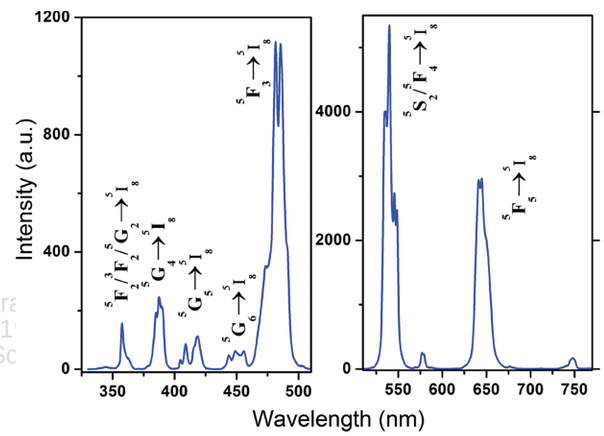

Figure 3. UC spectra of $NaYF_4$:20%Yb^{3+}, 1.5%Ho^{3+} MCs under 980 nm excitation.

The characteristic emissions of Ho^{3+} ions: $^3F_4/^5D_4 \rightarrow {}^5I_8$ (242.4 nm), $^3H_4/^5D_4/^1G_4 \rightarrow {}^5I_8$ (276.1 nm), $^5G_4/^5D_4/^3G_4 \rightarrow {}^5I_8$ (289.7 nm), $^3L_8/^3M_{10} \rightarrow {}^5I_8$ (296.4 nm), $^3P_1/^3D_3 \rightarrow {}^5I_8$ (303.6 nm), $^5F_2/^3F_2/^5G_2 \rightarrow {}^5I_8$ (357.7 nm), $^5G_4 \rightarrow {}^5I_8$ (387.8 nm), $^5G_5 \rightarrow {}^5I_8$ (418.7 nm), $^5G_6 \rightarrow {}^5I_8$ (449.6 nm),

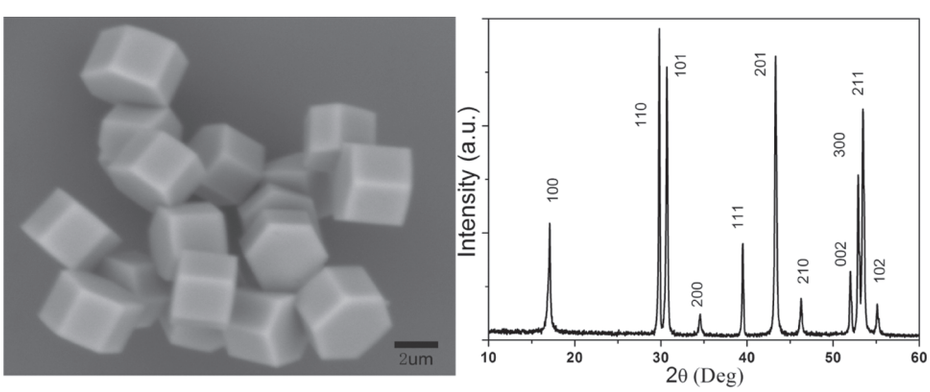

Figure 1. SEM and XRD pattern of $NaYF_4$:20%Yb^{3+}, 1.5%Ho^{3+} MCs.

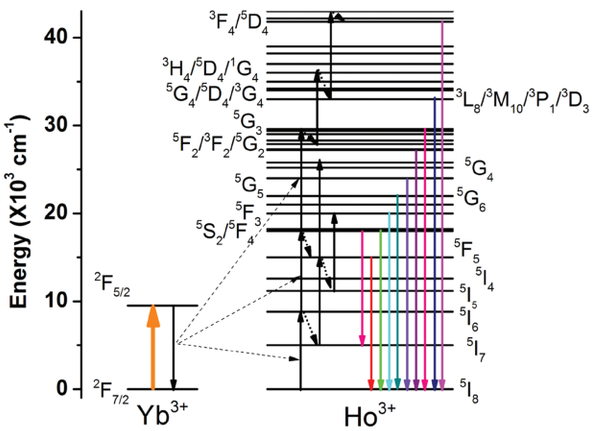

Figure 4. Energy level diagrams of Yb^{3+} and Ho^{3+} ions and possible UC emission processes.

$^5F_3 \rightarrow {}^5I_8$ (482.3 nm), $^5S_2/^5F_4 \rightarrow {}^5I_8$ (541.7 nm) and $^5F_5 \rightarrow {}^5I_8$ (644.5 nm) are presented here clearly.

Figure 4 shows the detailed UC processes of populations, relaxations, and emissions in the MCs. According to previous reports, the pump laser photons of 980 nm can only excite the Yb^{3+} ions, because the Ho^{3+} ions have no such excited levels above their ground state. As shown in Figure 4, three ET processes from Yb^{3+} to Ho^{3+} ions excite the $^5I_8$ to the $^5I_6$, $^4S_2/^5F_4$, and $^5G_3$ levels, with the redundant energy dissipated by phonons. Subsequent nonradiative relaxations of $^5G_3 \rightarrow {}^5F_2/^3F_2/^5G_2$ populate the $^5F_2/^3F_2/^5G_2$ levels. In the fourth-step excitation, the same laser pumps the excited-state atoms from the $^5F_2/^3F_2/^5G_2$ to the $^3H_4/^5D_4/^1G_4$ levels via ET and excited-state absorption (ESA). Then nonradiative relaxations of $^3H_4/^5D_4/^1G_4 \rightarrow {}^5G_4/^5D_4/^3G_4$ also populate the $^5G_4/^5D_4/^3G_4$ levels. In the fifth-step excitation, the same laser pumps the excited-state atoms from the $^5G_4/^5D_4/^3G_4$ to the $^3F_4/^5D_4$ levels via ET and ESA.

To understand the UC processes well, we investigated the excitation power dependence of UC luminescence intensities. For an unsaturated UC process, the integrated

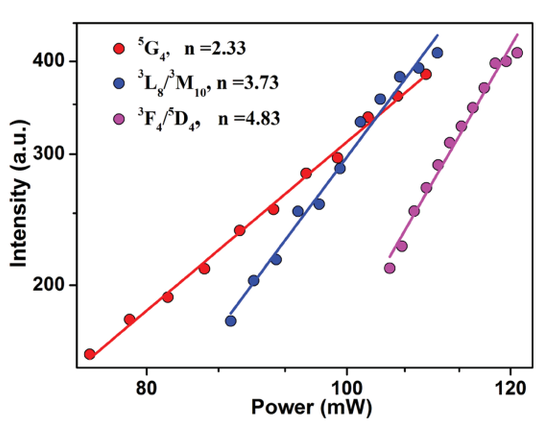

Figure 5. Excitation power dependence of UC luminescence in $NaYF_4$:20%Yb^{3+}, 1.5%Ho^{3+} MCs under 980 nm excitation.

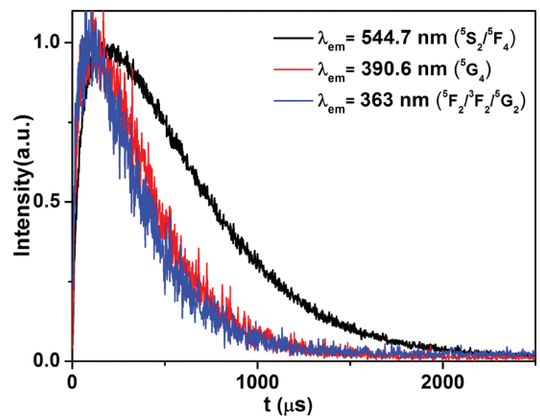

Figure 6. Temporal behaviors of emissions at 363 nm ($^5F_2/^3F_2/^5G_2$ levels), 390.6 nm ($^5G_4$ level) and 544.7 nm ($^5S_2/^5F_4$ levels) of Ho^{3+} ions under the excitation of 980 nm pulsed lasers.

Table I. Decay times of $^5G_4$, $^5S_2/^5F_4$ and $^5F_2/^3F_2/^5G_2$ levels of Ho^{3+} ions in $NaYF_4$:20%Yb^{3+}, 1.5%Ho^{3+} MCs calculated from the decay curves analysis.

Emitting level	$^5S_2/^5F_4$	$^5G_4$	$^5F_2/^3F_2/^5G_2$
Time taken for completion of decay τ (μs)	553	319	305

UC luminescence intensity I_f is proportional to P^n,[20] where P is the pumping laser power, and n is the number of laser photons required to populate the upper emitting state. Figure 5 shows the typical pump-power dependence of UC luminescence of $NaYF_4$:20%Yb^{3+}, 0.5%Ho^{3+}. The values of photon number n were 4.83, 3.73, and 2.33 for 242.4 nm ($^3F_4/^5D_4 \rightarrow {}^5I_8$), 289.7 nm ($^3L_8/^3M_{10} \rightarrow {}^5I_8$) and 387.8 nm ($^5G_4 \rightarrow {}^5I_8$) emission peaks of Ho^{3+} ions, respectively, indicating that these transitions were of five-, four-, and three-photon UC processes.

The temporal evolution of UC luminescence from Ho^{3+} ions in the MCs was studied. The decay curves of the UC fluorescence of Ho^{3+} ions were recorded under 953.6 nm pulsed Raman laser. For conciseness, only temporal evolutions of $^5F_2/^3F_2/^5G_2$, $^5G_4$, and $^5S_2/^5F_4$ levels of Ho^{3+} ions in $NaYF_4$:20%Yb^{3+}, 0.5%Ho^{3+} are given in Figure 6. These decay curves can be fitted well into single-exponential functions. The average lifetimes of all radiative levels are listed in Table I. As can be seen from Table I, the lifetimes are increasing along the ladder of the energy levels $^5F_2/^3F_2/^5G_2$, $^5G_4$ and $^5S_2/^5F_4$. This phenomenon indicates that in the Ho^{3+} ions, the higher the energy level locates, the more unstable the level is. These high-energy states prefer to de-excite to low-energy levels radiatively or nonradiatively due to the narrow energy gap between levels of Ho^{3+} ions.

4. SUMMARY

In conclusion, Yb^{3+}/Ho^{3+} codoped β-$NaYF_4$ MCs were synthesized through a facile EDTA-assisted hydrothermal

method. High-order UV UC emissions of Ho^{3+} ions were observed. Power-dependence analysis confirmed that these UV emissions of Ho^{3+} ions came from five-photon UC processes under 980 nm NIR light excitation.

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