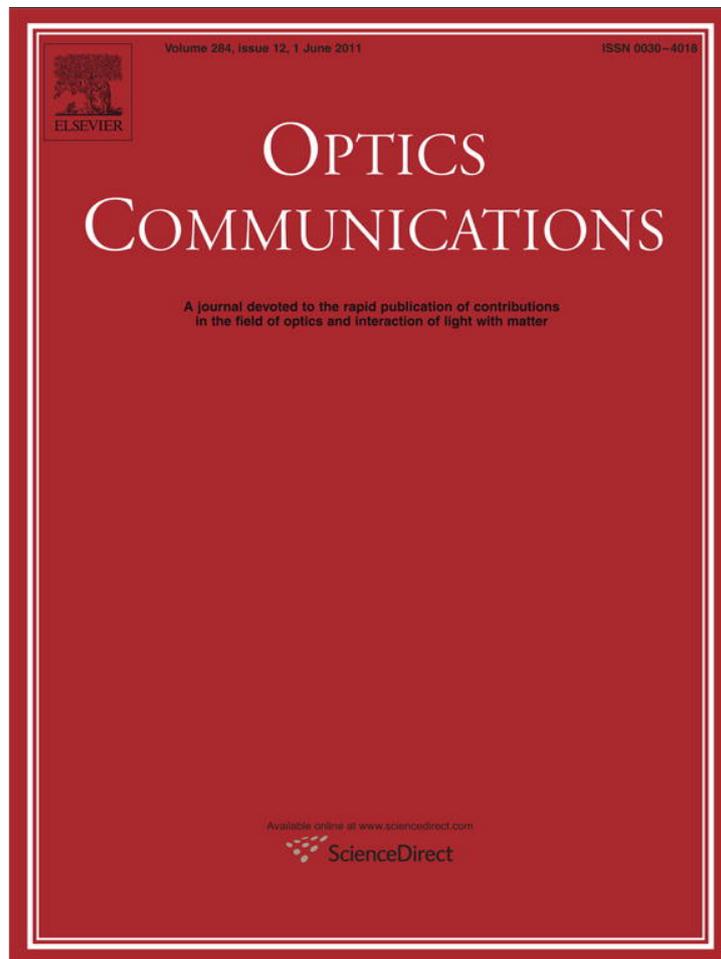


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Ultraviolet upconversion luminescence of Gd^{3+} from Ho^{3+} and Gd^{3+} codoped oxide ceramic induced by 532-nm CW laser excitation

Feng Qin^{a,b}, Yangdong Zheng^a, Ying Yu^a, Changbin Zheng^a, Poursadat Tayebi^a, Zhiguo Zhang^{a,b,*}, Wenwu Cao^{b,c,*}

^a Department of Physics, Harbin Institute of Technology, Harbin 150001, People's Republic of China

^b The Laboratory of Sono- and Photo-theranostic Technologies, Harbin Institute of Technology, Harbin 150001, People's Republic of China

^c Materials Research Institute, The Pennsylvania State University, University Park, PA 16802, United States

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ABSTRACT

Ultraviolet upconversion emissions around 314 nm from 6P_J states of Gd^{3+} ions have been observed in $Y_{1.98-x}Gd_xHo_{0.02}O_3$ ($x = 0.02, 0.10, 0.20$, and 0.30) oxide ceramics under the excitation of a continuous-wave 532-nm laser. We found that the energy transfer process from Ho^{3+} to Gd^{3+} plays an important role in populating the 6P_J states of Gd^{3+} . The doping of Gd^{3+} ions does not affect 5G_4 and 5G_5 states but only the 3D_3 state of Ho^{3+} . The emissions from 3D_3 state decrease with the increase of Gd^{3+} concentration. Power dependence curves and time-resolved spectra have been measured to identify the proposed upconversion mechanism.

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1. Introduction

Potential applications in environmental sciences, medicine, photolithography, material processing, high-density optical data storage and many others have stimulated the development of ultra-violet (UV) solid-state lasers [1,2]. Frequency upconversion (UC) in optical generation is an important mechanism to produce short wavelength laser by certain rare-earth ions, pumped with a relatively longer wavelength laser by means of intrinsic energy level matching. In this way, high-lying excited states are populated by multi-photon processes such as excited state absorption (ESA), energy transfer upconversion (ETU) and photon avalanche (PA) absorption [3].

Rare earth ions have ample electronic state levels and have been widely used as activators in UC materials. Er, Tm, Ho, Pr, etc. have been studied extensively for their luminescence in visible and UV regions. Trivalent gadolinium ions (Gd^{3+}) have a $4f^7$ configuration for which the energy gap between the ground state ${}^8S_{7/2}$ and the first excited state ${}^6P_{7/2}$ is $32\,000\text{ cm}^{-1}$. Spectral properties of Gd^{3+} ions have been theoretically and experimentally studied, especially by vacuum UV (VUV) excitation [4–8]. However, UC emissions from Gd^{3+} ions have rarely been reported due to the large energy gap. In $CsMgCl_3$ crystals, Gharavi and McPherson observed 281 and 313 nm UC emissions from Gd^{3+} ions which were sensitized by Er^{3+} ions under green pulse laser excitation [9]. Cao et al. obtained the shortest wavelength (246.2 nm)

on record of UC emissions utilizing Tm^{3+} and Yb^{3+} as sensitizers in fluoride hosts under the excitation of a 980 nm laser [8].

In this paper, we report an observation of UC emissions from Gd^{3+} ions in Gd^{3+} – Ho^{3+} codoped Y_2O_3 ceramic. Ho^{3+} ions acted as sensitizers in the luminescence of Gd^{3+} . With a continuous-wave (CW) 532-nm solid state laser as the excitation source, Ho^{3+} ions absorbed pump photons and transferred the energy to Gd^{3+} , which resulted in the UV emissions.

2. Experiment and discussion

The starting materials were all analytical reagents. A series of $Y_{1.98-x}Gd_xHo_{0.02}O_3$ ($x = 0, 0.02, 0.10, 0.20$, and 0.30) samples were synthesized by the traditional sol–gel method. The resulting nanocrystals were pressed under 100 MPa pressure into smooth and flat disks, then sintered at $1300\text{ }^\circ\text{C}$ for 32 h in air to form a ceramic [10].

X-ray diffraction showed that the samples are all in a single phase and have a cubic structure. The ceramic samples were excited by a 532-nm laser (CLO Laser DPGL-500L), and the resulting emissions were analyzed using a monochromator (Zolix SBP300) with the resolution of 1 nm. Florescence in the UV and visible ranges were amplified by a photomultiplier tube (Zolix CR131) and the signals were recorded on a chart recorder (Zolix DSC102). In order to measure the fluorescence lifetime, the CW laser was modulated by an electro-optic modulator (Leysop EM200K) with square wave modulation. The induced time-resolved curves were recorded by a digital phosphor oscilloscope (Tektronix TDS 5052).

* Corresponding authors at: The Laboratory of Sono- and Photo-theranostic Technologies, Harbin Institute of Technology, Harbin 150001, People's Republic of China. E-mail addresses: zhangzhiguo@hit.edu.cn, dzk@psu.edu (Z. Zhang).

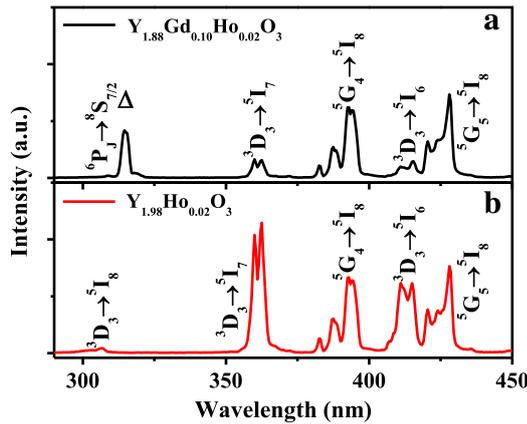


Fig. 1. Upconversion emission spectra of $Y_{1.88}Gd_{0.10}Ho_{0.02}O_3$ (a) and $Y_{1.98}Ho_{0.02}O_3$ (b) under the 532-nm laser excitation.

By the excitation of 532-nm solid state laser with a pump power of 400 mW, the oxide ceramic $Y_{1.88}Gd_{0.10}Ho_{0.02}O_3$ emitted strong UV fluorescence, as shown in Fig. 1(a). Three emission bands in the range of 300–330 nm came from the ${}^6P_J \rightarrow {}^8S_{7/2}$ transitions of Gd^{3+} . The luminescence that peaked around 392 and 428 nm originated from ${}^5G_4 \rightarrow {}^5I_8$, and ${}^5G_5 \rightarrow {}^5I_8$ transitions of Ho^{3+} , respectively. Another two relative weaker emissions centered at 362 and 412 nm were also from Ho^{3+} , which can be assigned to the transitions of ${}^3D_3 \rightarrow {}^5I_6$ and ${}^3D_3 \rightarrow {}^5I_7$, respectively [11,12].

Fig. 2 is the energy level diagram of Gd^{3+} and Ho^{3+} ions [5,12,13]. In the Gd^{3+} – Ho^{3+} codoped system, Ho^{3+} ions in the ground state absorbed the pumping photons of the CW laser and populate the coupled ${}^5S_2/{}^5F_4$ states by the GSA process. Subsequently, the 3D_3 state was populated by both the ETU and ESA processes, using ${}^5S_2/{}^5F_4$ states as the intermediate state [11]. Due to the large energy gap between the ground state ${}^8S_{7/2}$ and the first excited state 6P_J , Gd^{3+} ions cannot absorb the 532 nm photons directly. However, because the population of the 3D_3 state of Ho^{3+} ions, the 6P_J states of Gd^{3+} could be populated through the energy transfer between Ho^{3+} and Gd^{3+} ions: ${}^3D_3 \rightarrow I_8$ (Ho^{3+}): ${}^8S_{7/2} \rightarrow {}^6P_J$ (Gd^{3+}). In order to further prove the energy

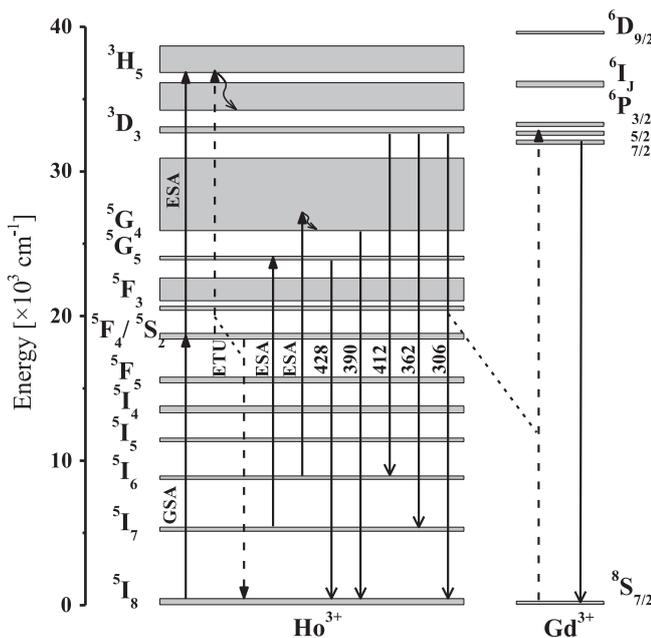


Fig. 2. Partial energy-level diagrams of Ho^{3+} and Gd^{3+} ions and the proposed upconversion emission mechanism.

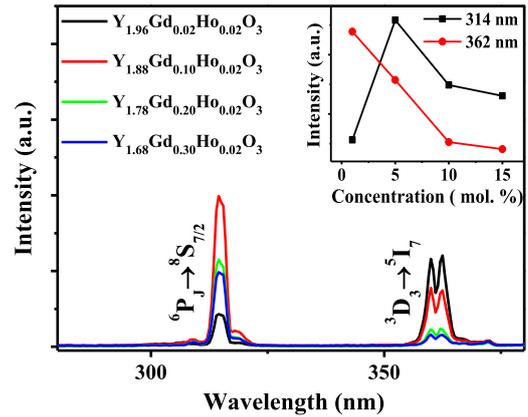


Fig. 3. Upconversion emission spectra of $Y_{1.96-x}Gd_{0.02}Ho_{0.02}O_3$ ($x = 0.02, 0.10, 0.20,$ and 0.30). The inset is the integrated upconversion emission intensities versus Gd^{3+} ion concentration.

transfer process from Ho^{3+} to Gd^{3+} , we compared the emission spectra of $Y_{1.88}Gd_{0.10}Ho_{0.02}O_3$ and $Y_{1.98}Ho_{0.02}O_3$, as shown in Fig. 1. The emission of Gd^{3+} was marked with a triangle (Δ). The spectra were all measured under the same conditions (both incident and exit slits of the monochromator are 0.25 mm wide, the high voltage of the photomultiplier tube is 750 V and the pump power is 400 mW). We can see from Fig. 1 that the doping of Gd^{3+} ions has little effect on the emissions from 5G_4 and 5G_5 states but only on 3D_3 state. Based on the spectral analysis, the populations of the excited states 6P_J of Gd^{3+} are induced by the energy transfer process between excited Ho^{3+} and Gd^{3+} ions. Furthermore, the reduction of the emissions from 3D_3 state also offered evidence for the referred energy transfer process.

In order to increase the UV efficiency of emissions from Gd^{3+} , we have optimized the host material by adjusting their compositions. Fig. 3 shows upconversion emission spectra of $Y_{1.98-x}Gd_xHo_{0.02}O_3$ ($x = 0.02, 0.10, 0.20,$ and 0.30) samples, which were all measured under the same conditions. The inset in Fig. 3 shows the integrated emission intensity versus Gd^{3+} ions concentration. With the increase of Gd^{3+} concentration, emissions from Gd^{3+} first increased then decreased after passing the peak concentration of 5% mol, while the emissions from 3D_3 state of Ho^{3+} always decreased, which offered evidence for the energy transfer from Ho^{3+} to Gd^{3+} . Moreover, the variation of fluorescence intensity in the spectra implies that there could be concentration quenching between Gd^{3+} ions [7].

The temporal evolution of Gd^{3+} fluorescence was studied and the decay curves for the representative emission (314.5 nm) from 6P_J state were recorded as shown in Fig. 4. The decay curves can be fitted well to an exponential function $I = I_0 \exp(-t/\tau)$. According to the best-fit in Fig. 4, the lifetime of 6P_J state is 850 (20), 460 (20), 130 (20), 81 (10) μs for $Y_{1.98-x}Gd_xHo_{0.02}O_3$ ($x = 0.02, 0.10, 0.20,$ and 0.30), respectively. To interpret the change in the fluorescence of Gd^{3+} with the increase of the doping concentration, a simplified model is proposed. The parameters used are defined as follows: A_{10} is the radiative transition probability of 6P_J levels, c is the coupling parameter of energy transfer process, $n_2, n_0,$ and n_1 are the population of the ${}^3D_3, {}^8S_{7/2}$ and 6P_J levels, respectively. Also n_0 could be considered as the doping concentration of Gd^{3+} ions. Since the co-doped system is under a steady-state excitation, n_2 could be treated as a constant. Based on the conservation of particle-number for 6P_J levels, we have $n_2 n_0 = n_1 A_{10} + c' n_1 n_0$, where c' is the interaction parameter for energy transfer process. Therefore, for the emission of 6P_J levels, we have

$$n_1 A_{10} = \frac{c n_2 n_0 A_{10}}{A_{10} + c' n_0} = c n_2 n_0 A_{10} \tau_1 \propto n_0 \tau_1, \quad (1)$$

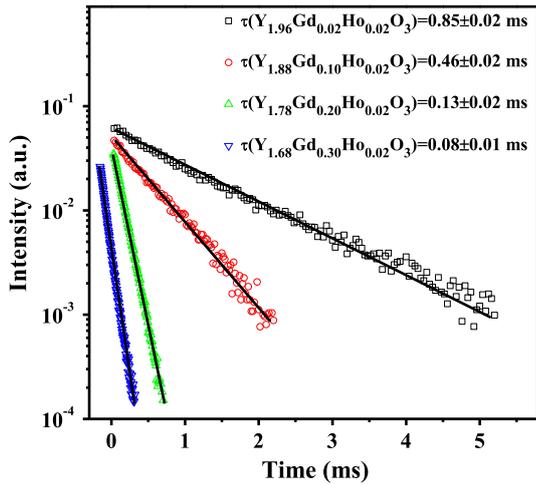


Fig. 4. Time evolution curves for the 314 nm emissions of Gd^{3+} in $Y_{1.98-x}Gd_xHo_{0.02}O_3$ ($x = 0.02, 0.10, 0.20,$ and 0.30).

where $\tau_1 = \frac{1}{A_{10} + c n_0}$ is the measured fluorescence lifetime of the 6P_1 levels. Eq. (1) means that the emission intensity is proportion to the product of the doping concentration n_0 and the measured fluorescence lifetime τ_1 , which is in accordance with the experimental results shown in Fig. 5.

To better understand the physical mechanisms responsible for the observed upconversion emissions described above, the emission intensities were measured as a function of the pumping power. For an unsaturated upconversion process, the upconverted emission intensity (I_{em}) depends on the pumping laser power (I_{pump}) according to the following relation:

$$I_{em} \propto I_{pump}^n, n = 2, 3, \dots \quad (2)$$

where n is the number of pumping photons absorbed per short wavelength photon emitted [10]. Fig. 6 shows a typical logarithmic plot of the integrated upconverted emission intensities versus the pumping power. The fluorescence intensity was represented by the integrated area between the corresponding spectral profile and the baseline. The n values could be easily evaluated from the slope of the linear fit, as illustrated in Fig. 6. For the emission from Gd^{3+} peaked at 314 nm, the obtained n values were all around 1.5 (± 0.1) for the $Y_{1.98-x}Gd_xHo_{0.02}O_3$ ($x = 0.02, 0.10, 0.20,$ and 0.30) series, which indicated that two-photon processes were responsible for the population of 6P_1 states.

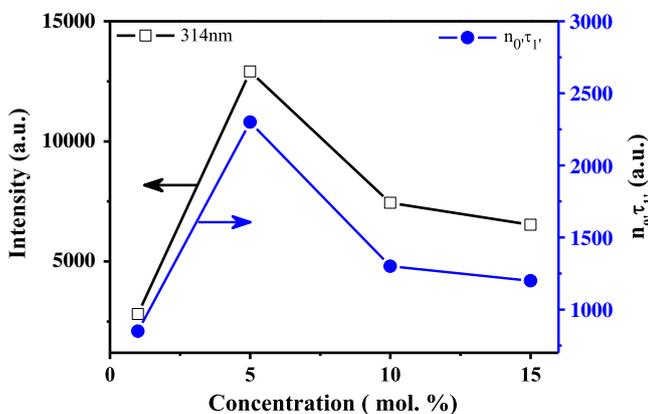


Fig. 5. Concentration dependence of fluorescence intensities of Gd^{3+} and the product of the doping concentration and the lifetime.

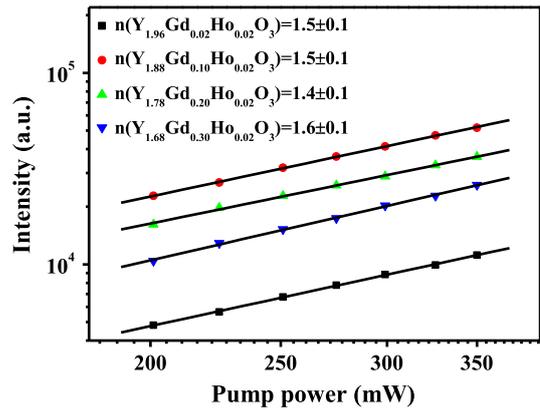


Fig. 6. Logarithmic plot of laser power versus upconversion emission intensity for the 314 nm emissions of $Y_{1.98-x}Gd_xHo_{0.02}O_3$ ($x = 0.02, 0.10, 0.20,$ and 0.30) under the 532-nm laser excitation.

In order to analyze the above physical processes, differential equations of states are proposed as following:

$$\frac{dn_1}{dt} = \sigma_{01}\rho n_0 - n_1 A_1 - \sigma_{12}\rho n_1 - W n_1^2 \quad (3a)$$

$$\frac{dn_2}{dt} = \sigma_{12}\rho n_1 + W n_1^2 - n_2 A_2 - c n_0 n_2 \quad (3b)$$

$$\frac{dn_{1'}}{dt} = c n_0 n_2 - n_{1'} A_{1'} \quad (3c)$$

where n_0 and n_1 are the population of the 5I_8 and ${}^5S_2/{}^5F_4$ levels, respectively, σ_{ik} is the absorption cross section between the i and k states, A_{ik} is the radiative transition probability, ρ is the pumping energy density, and W is the corresponding parameter of ETU process. For the 6P_1 state, under the steady-state excitation, we have

$$n_{1'} A_{1'} = \frac{A_{10'} c n_0 (\sigma_{12} \rho n_1 + W n_1^2)}{A_{1'} (A_2 + c n_0)} \quad (4)$$

When $n_1 A_1 \gg \sigma_{12} \rho n_1 + W n_1^2$, i.e., when linear decay dominates the ${}^5S_2/{}^5F_4$ states, the upconversion term in Eq. (3a) is negligible, so that $n_1 A_1 = \sigma_{01} \rho n_0$, and $n_{1'} A_{1'} \propto \rho^2$. When $n_1 A_1 \ll \sigma_{12} \rho n_1 + W n_1^2$, i.e., when the upconversion is dominant for ${}^5S_2/{}^5F_4$ states, the linear decay term in Eq. (3a) is negligible, and we have $\sigma_{12} \rho n_1 + W n_1^2 = \sigma_{01} \rho n_0$, then $n_{1'} A_{1'} \propto \rho$. Therefore, in our case, for the ${}^5S_2/{}^5F_4$ states, upconversion is a depletion mechanism comparable with linear decay [14].

3. Conclusion

In conclusion, $Y_{1.98-x}Gd_xHo_{0.02}O_3$ ($x = 0.02, 0.10, 0.20,$ and 0.30) ceramics were synthesized using a sol-gel method. The ceramic emitted intense UV luminescence under 532 nm CW laser excitation. The experimental data indicated that the excited Ho^{3+} ions successfully transferred their energy to surrounding Gd^{3+} ions. Intense UV UC emissions from the long-lifetime of Gd^{3+} doped oxide ceramic $Y_{1.98-x}Gd_xHo_{0.02}O_3$ ($x = 0.02, 0.10, 0.20,$ and 0.30) make the ceramic material a potential candidate for building compact UV solid-state lasers.

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