Unusual power-dependent and time-dependent upconversion luminescence in nanocrystals Y_2O_3: Ho^{3+}/Yb^{3+}

Linmei Yang, Hongwei Song*, Lixin Yu, Zhongxin Liu, Shaozhe Lu

Key Laboratory of Excited State Physics, Changchun Institute of Optics, Fine Mechanics and Physics, Chinese Academy of Science, 16 East Nan-Hu Road, Changchun, Jilin 130033, P. R. China

Abstract

The unusual power-dependent and time-dependent upconversion luminescence (UCL) in nanocrystals Y_2O_3: Ho^{3+}/Yb^{3+} was reported under 978-nm excitation. It was observed that the UCL intensity increased as the excitation power increased under lower excitation density, but decreased in the case of higher excitation density. At lower excitation density, the intensity solely increased with exposure time. As the excitation density reached a certain value, a maximum of intensity appeared as a function of time. Under higher power density, the intensity solely decreased with time. Similar phenomenon was also observed in Er^{3+}-doped and Tm^{3+}-doped samples. The origin of unusual power- and time-dependent UCL was discussed.
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1. Introduction

The upconversion from infrared to shorter wavelength in materials doped with trivalent-rare-earth (RE) ions such as Er^{3+}, Tm^{3+}, Ho^{3+}, Nd^{3+}, and Pr^{3+} has attracted considerable interest for more than three decades [1–3]. Recently, the availability of high-power infrared laser diodes has stimulated research in the areas of upconversion pumped visible laser, light emitting devices, and three-dimensional displays. In 2000 Capobianco et al. reported the NIR-to-visible upconversion in erbium-doped nanocrystalline yttria for the first time [4]. Later D. Matsuura et al. also observed strong upconversion luminescence (UCL) in trivalent RE (RE = Er^{3+}, Tm^{3+}) -doped yttria nanocrystals [5]. Since the publication of these reports, infrared to visible UCL in nanocrystals has attracted considerable attention due to its

Corresponding author. Tel./fax: +864316176320.
E-mail address: songhongwei2000@sina.com (H. Song).

potential application in infrared detection, molecule recognition and three-dimensional displays [6–8]. It is well known that Ho^{3+} is a suitable active ion for the upconversion laser and the Ho^{3+}–Yb^{3+} is also a highly efficient UCL system [9–12]. However, the report on UCL of Ho^{3+}–Yb^{3+} codoped nanocrystals is quite rare until now. In addition, the dependence of UCL intensity on pump power in nanoparticles was not well studied. Considering the above two points, the UCL, especially the powerdependence of UCL in nanocrystalline Y_2O_3: Ho^{3+}/Yb^3 was studied. It is very interesting to observe the unusual power-dependent and time-dependent characteristic of UCL in Y_2O_3: Ho^{3+}/Yb^3 nanoparticles. To definitely explore its origin, the EPR spectra were performed.

2. Experiments

Nanosized cubic Y_2O_3: Ho^{3+} (2 mol%)/Yb^{3+} (1 mol%) crystals were prepared by the solution combustion synthesis procedure that was originally reported by Y. Tao et al. [13]. In the preparation, stoichiometric $Y(NO_3)_3$, $Ho(NO_3)_3$, $Yb(NO_3)_3$ and glycine were dissolved in distilled water and mixed to form the precursor solution. Then the solution was concentrated by heating until excess water evaporated completely and spontaneous ignition occurred. The resultant Y_2O_3: Ho/Yb powders were formed after the combustion was finished. The synthesis reaction is

$$6M(NO_3)_3 + 10NH_2CH_2COOH + 18O_2$$

$$\rightarrow 3M_2O_3 + 5N_2 + 18NO_2 + 20CO_2 + 25H_2O,$$
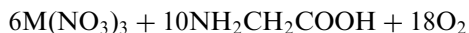
where M = Y, Yb, Ho. To improve the crystallinity of the nanocrystalline powders and eliminate redundant nitrate, they were annealed at 500 °C for 2 h. The particle size was controlled by adjusting the molar ratio of glycine to metal nitrate (G/N) which had an effect on the combustion temperature in the reacting process.

Crystal structure and size were obtained by X-ray diffraction (XRD) patterns. In UCL experiments, a 978 nm diode laser having a power

maximum of 2 W was used to pump the samples. The spectra were recorded by a monochromater, a TR550 grating spectrometer and a computer. Time scan spectra of emission intensity were collected by a Hitachi F-4500 fluorescence spectrometer. The EPR spectra were measured by a JES-FE3AX EPR spectrometer with a central magnetic field intensity of 3368 G and scanning scope of 5000 G.

3. Results and discussion

Fig. 1 shows the XRD of different nanoparticles. According to JCPDS standard cards, all the nanoparticles exhibit pure cubic structure. The particle sizes were estimated from the half-width of the peaks of the XRD patterns by using the Scherrer's formula [14] and found to be 8, 13, 20 and 55 nm, respectively.

Fig. 2(a) shows the UCL spectra under 978-nm excitation. The green emissions near 549 nm and the red emissions near 668 nm were observed, which were associated with the $^5S_2/^5F_4$–$^5I_8$ and $^5F_5$–$^5I_8$ transitions of Ho^{3+}, respectively. It appeared that the total emission intensity decreased and the intensity ratio of red emissions to green emissions increased with the decreasing
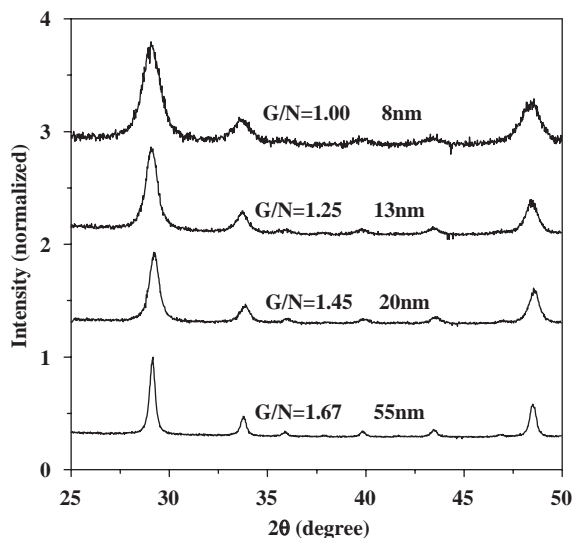

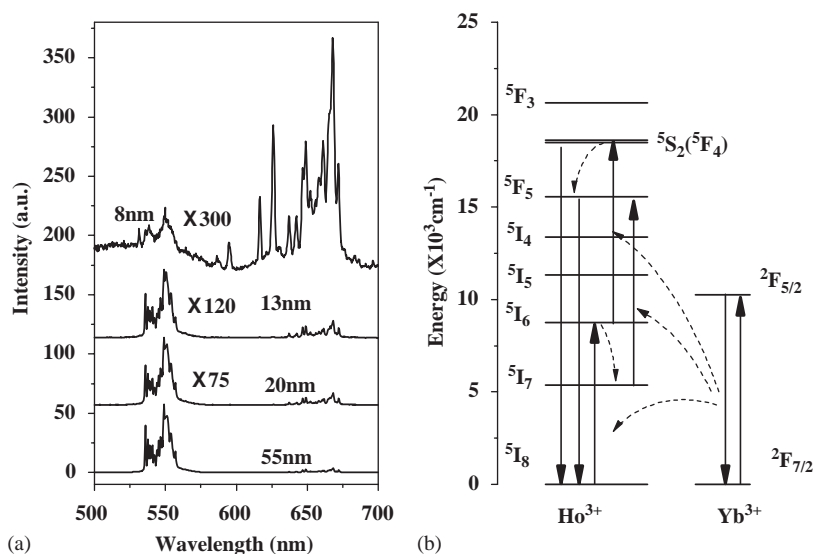Fig. 1. XRD patterns of different size Y_2O_3: Ho^{3+}/Yb^{3+}.

Fig. 2. (a) UCL spectra of different size Y_2O_3:Ho^{3+}/Yb^{3+} (λ_{ex} = 978 nm). (b) The energy level diagrams of Ho^{3+} and Yb^{3+}.

particle size. Fig. 2(b) shows the energy level diagrams of Ho^{3+}/Yb^{3+} and the UCL processes under 978-nm excitation. Firstly, the ground state electrons of $^5I_8$ are excited to $^5I_6$ through the energy transfer of $Yb^{3+} \rightarrow Ho^{3+}$ or ground state absorption. In this process, the energy transfer of $Yb^{3+} \rightarrow Ho^{3+}$ should be dominant because of strong ground state absorption at 978 nm for Yb^{3+} and much stronger emission intensity in Yb^{3+}/Ho^{3+} codoped nanocrystals in comparison to that in Ho^{3+}-doped ones. Some electrons on $^5I_6$ are excited to $^5S_2$/$^5F_4$ through energy transfer or excited state absorption, generating the green emissions of $^5S_2$/$^5F_4$–$^5I_8$, while the others relax into $^5I_7$ and then are excited to $^5F_5$ through energy transfer or excited state absorption, generating the red emissions of $^5F_5$–$^5I_8$. The nonradiative relaxation of $^5S_2$/$^5F_4$–$^5F_5$ is the other path for populating the red $^5F_5$ level. In the populating process of the red emissions, the nonradiative relaxation of $^5I_6$–$^5I_7$ and $^5S_2(^5F_4)$–$^5F_5$ are involved. The non-radiative relaxation rate increases dramatically with the decrease of particle size due to a great number of surface defects such as CO_3^{2-} and OH^- which possess the vibrational energies of 1500 and 3300 cm^{-1}, respectively [8]. The increase of non-radiative relaxation leads to the quenching of total

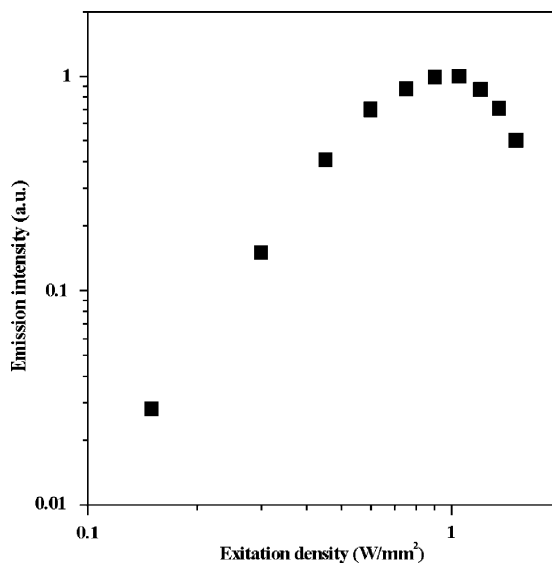Fig. 3. UCL intensity vs. excitation density in 55-nm Y_2O_3:Ho^{3+}/Yb^{3+} (λ_{em} = 549 nm).

emission intensity and the relative increase of the red emissions [15,16].

Fig. 3 shows a typical dependence of UCL intensity on excitation density. It can be seen that as the excitation power density was lower than

$1\,W/mm^2$, the emission intensity increased with the increasing power density. As the power density reached $1\,W/mm^2$, the emission intensity approached a maximum, and then decreased as the power density increased continuously. The dependence of luminescence intensity at 549 nm on exposure time under different excitation densities was also measured, as shown in Fig. 4. It can be seen that the UCL intensity solely and slightly increased with time as the excitation density was or lower than $0.15\,W/mm^2$. As the excitation density reached $0.3\,W/mm^2$, the emission intensity increased with time initially, and then approached a maximum at a certain time, and finally decreased with time. As the power was higher than $0.9\,W/mm^2$, the emission intensity solely decreased. The higher the excitation density, the larger the relative intensity decrease, and faster is the response time. The inset shows log–log plot of the relative change as a function of excitation density. In the figure, the slope is determined to be 1.95, suggesting that the relative intensity change maybe a two-photon or multi-phonon process. The above experiments

Fig. 4. Normalized emission intensity vs. excitation time under different excitation density in 55-nm Y_2O_3: Ho/Yb: (a) $0.15\,W/mm^2$; (b) $0.3\,W/mm^2$; (c) $0.9\,W/mm^2$; (d) $1.5\,W/mm^2$. Inset: log–log plot of the relative change vs. excitation density ($\lambda_{em} = 549\,nm$).

were repeatedly performed and confirmed in different samples.

As early as in 1960s, Singh and J. E. Geusic observed the "saturation" phenomenon of an UCL for higher pump powers [17]. Later, M. Pollnau et al. investigated the physical nature of the "saturation" phenomenon. They observed that the dependence of an UCL intensity on pump power decreased in slope with increasing excitation and gave a theoretical model considering the competition between linear decay and upconversion processes for the depletion of the intermediate excited states [18]. Our present experimental results were inconsistent with theirs, so its physical nature should also be different. There are several probabilities leading to the unusual power-dependent and time-dependent upconversion luminescent behavior. (1) Thermal effect: Yb^{3+} has relative strong absorption around 978 nm in the Y_2O_3 host. As excitation density was high enough, the strong absorption led the nanocrystal temperature to increase, inducing thermal quenching of the photoluminescence. If thermal effect contributed to the unusual dependence dominantly, the intensity variation should be strongly dependent on Yb^{3+} concentration. However, the experimental results indicated that the decrease of emission intensity with power and time is independent of Yb^{3+} concentration. (2) Accompanied photostimulated luminescence (PSL): Dhanaraj et al. observed the thermal stimulated luminescence (TSL) in both Y_2O_3: Eu nanoparticles and the bulk ones [19]. They considered that the TSL in Y_2O_3: Eu originated from the combination of released electrons from oxygen vacancies with some luminescent centers. Actually, the electrons trapped in oxygen vacancies can be also be photostimulated and combine with luminescent centers such as Ho^{3+} if the photon energy is high enough. Eventhough PSL exists indeed, it can not be distinguished from UCL under 980-nm excitation. Under the 808-nm excitation, UCL can be avoided, because the 808-nm light is not in resonance with any transitions of Yb^{3+} or Ho^{3+}. To examine whether the PSL exists or not, the samples were excited under 808 nm diode laser after having been exposed under the ultraviolet light (254 nm) or the X-ray for 40 min. The
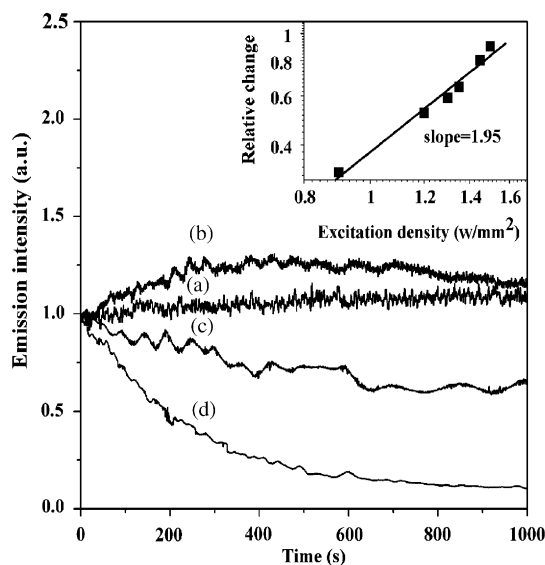
ultraviolet or X-ray irradiation can lead more electrons to be captured by defect levels. The electrons in defect levels will be released through photo-stimulation of the 808-nm light and recombine with luminescent centers, inducing PSL. However, we did not observe any visible PSL at all, suggesting that the proposed PSL process hardly happened. (3) Light-induced structural change: In previous papers, we reported ultraviolet and visible light-induced luminescent decrease in Y_2O_3: Eu nanocrystals [20] and luminescent enhancement in Y_2O_3: Tb nanocrystals [21]. In Y_2O_3: Eu and Y_2O_3: Tb, the spectral change strongly depended on particle size, and thus was attributed to the rearrangements of local environments around the Eu or Tb ions in/near the surface of nanoparticles [20,21]. But in the present luminescent decrease in Y_2O_3: Ho, Yb is independent of particle size, indicating that it is not assigned to the surface effect. Therefore, if the unusual power- and time-dependent UCL is related to the local structural change surrounding Ho^{3+} ions, it should be related to the structural change not only for the surface Ho^{3+} ions, but also for the inner Ho^{3+} ions.

To definitely reveal the origin, the EPR experiments were performed. Fig. 5 shows the EPR spectra of Y_2O_3 and Y_2O_3: Ho^{3+}/Yb^{3+} before and after exposure under 978-nm laser. In the undoped Y_2O_3, a broad EPR signal appeared between 3000 and 3500 G, which was attributed to the oxygen vacancies in the Y_2O_3 host [20], and the signal had little variations after irradiation. In the Y_2O_3: Ho^{3+}, Yb^{3+} before exposure, the same signal appeared and the strength had little variation. After exposure, a new signal appeared, with a central position of 3018 G, line width of 50 G, and a g factor of 2.2338. The signal was unstable and disappeared quickly and thus can not be obtained repeatedly. Presently, it is hard for us to identify its origin. We guess there is a possibility that after intense laser irradiation some Yb^{3+}/Ho^{3+} changed to the other valence states through electronic tunneling processes. The reduction of Yb^{3+}/Ho^{3+} in excited states could be responsible for the decrease of emission intensity and the signal maybe originating from holmium and yttrium in other valence states. The possibility of charge
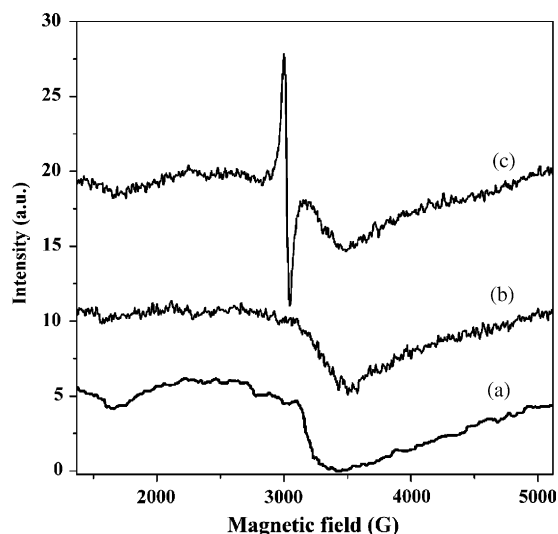

Fig. 5. EPR spectra of 55-nm Y_2O_3 and Y_2O_3: Ho^{3+}/Yb^{3+} before and after exposure with 978-nm laser: (a) undoped Y_2O_3 before exposure; (b) Y_2O_3: Ho^{3+}/Yb^{3+} before exposure; (c) Y_2O_3: Ho^{3+}/Yb^{3+} immediately after exposure for 20 min.

transfer change for Yb^{3+} is larger, because the unusual power-dependent UCL was also observed in Er^{3+}/Yb^{3+} codoped and Tm^{3+}/Yb^{3+} codoped samples. However, we could not obtain any literature on the stable existence of the other valence states of holmium and yttrium. In one word, presently we cannot clarify the origin of the interesting time-dependent and intensity-dependent UCL. In Tm^{3+}-doped and Er^{3+}-doped Y_2O_3 nanoparticles also, similar experimental results were observed.

4. Conclusions

In summary, we reported the observation of unusual power-dependent and time-dependent UCL in nanocrystals Y_2O_3: Ho^{3+}/Yb^{3+} under the excitation of 978-nm laser. It was observed that the UCL intensity increased as the excitation power increased under lower excitation density, but decreased in the case of higher excitation density. And the luminescence intensity decreased with time under high excitation density. Now what is the origin of the unusual power-dependent and time-dependent UCL is not clarified: thermal

effect, accompanied PSL, structural change or valence state transfer of rare earth ions? Further work should be performed to clarify its origin.

Acknowledgments

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