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Upconversion Luminescence Dynamics in Er^{3+}/Yb^{3+} Codoped Nanocrystalline Yttria *

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The upconversion luminescence and dynamics in Er^{3+}/Yb^{3+} codoped nanocrystalline yttria (7–65 nm) are studied under 980-nm pulsed laser excitation. It is found that the red emission of $^4F_{9/2}$–$^4I_{15/2}$ and the green emission of $^2H_{11/2}/^4S_{3/2}$ in nanoparticles with lower concentration of Yb^{3+} result from a two-photon excitation. In nanocrystals with higher Yb^{3+} concentration, the red emissions from a two-photon excitation, while the green emissions from a three-photon excitation. The luminescence dynamics indicates that as the particle size decreases, both the rise and the decay time constants become shorter. As the size decreases to several nanometres, the rise process nearly disappears, suggesting that the upconversion luminescence originates mainly from self-excitation of Er^{3+}, instead of the energy transfer of $Yb^{3+} \rightarrow Er^{3+}$.

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Infrared-to-visible upconversion luminescence in nanocrystals has attracted considerable attention since Matuura reported strong upconversion luminescence in trivalent rare-earth doped yttria nanocrystals.[1−3] Phosphors in the nanoscale with high luminescent efficiency have potential applications in some fields such as high-resolution three-dimensional display, IR detection and molecule recognition. In the past, the bulk upconversion luminescence materials doped with Er^{3+} ions and sensitized with Yb^{3+} ions has been widely studied, because not only Er^{3+} ions have energy levels capable of infrared pumping that closely matches the most attractive 980-nm laser diode (LD) wavelength but also this wavelength region is in fair agreement with the peak wavelength of Yb^{3+} absorption.[4−10] Recently, several authors reported the upconversion luminescence properties of Er^{3+}-doped or Er^{3+}/Yb^{3+}-codoped yttria (Y_2O_3). It has been interesting to observe that the intensity ratio of the red emission to green emission varies greatly as the particle size changes from bulk to nanoscale.[3] This indicates that the populating processes for particles with different sizes are greatly changed. To better understand the difference of the luminescent processes between the bulk and the nanoparticles, the luminescent dynamics must be well studied. However, the upconverted luminescence in nanoparticles is relatively new and little research has been reported. In this Letter, we demonstrate the size-dependent upconversion luminescence and dynamics in Er^{3+}/Yb^{3+}-codoped Y_2O_3 nanocrystals.

Nanosized cubic Y_2O_3 crystals doped with 1 mol% of Er_2O_3 and 1, 3, 5, 8, 10 mol% of Yb_2O_3 ($Y_{1.98}Er_{0.02}O_3$, $Y_{1.96}Yb_{0.02}Er_{0.02}O_3$, $Y_{1.92}Yb_{0.06}Er_{0.02}O_3$, $Y_{1.88}Yb_{010}Er_{0.02}$, $Y_{1.82}Yb_{0.16}Er_{0.02}O_3$, $Y_{1.78}Yb_{0.20}Er_{0.02}O_3$) were prepared by using a solution combustion synthesis procedure. Details of the synthesis have been given elsewhere.[11] Luminescence spectra and dynamics were measured by exciting with 980 nm using an optical parameter oscillator (OPO) laser pumped by a pulsed Nd:YAG laser with a pulse duration of 10 nm, repetition frequency of 10 Hz. The signal was recorded by using a monochromator, a Boxcar averager and a computer.

Figure 1(a) shows the upconversion luminescence spectra in the nanoparticles with different sizes. Green emission of $^2H_{11/2}/^4S_{3/2}$–$^4I_{15/2}$ and red emissions of $^4F_{9/2}$–$^4I_{15/2}$ were observed. It is obvious that the emission intensity decreases with the decreasing particle size. On the other hand, the intensity ratio of the red emission to the green emission increases with the decreasing particle size. Figure 1(b) shows the upconversion luminescence spectra in the 65-nm particles with different Yb^{3+} concentrations. As the Yb^{3+} concentration increases, the red-emission intensity increases. In contrast, the green-emission intensity decreases. It should be noted that the blue emission of $^4H_{9/2}$–$^4I_{15/2}$ was also observed.[11]

Figures 2(a) and 2(b) show the logarithm plots of the emission intensity of $Er_{0.02}Yb_{0.02}Y_{1.96}O_3$ and $Er_{0.02}Yb_{0.20}Y_{1.78}O_3$ powders of about 65 nm as a function of excitation power. For nanoparticles with lower concentration of Yb^{3+}, both the red and green emissions yield a slope of ∼2, indicating that the population on the red and the green levels is a two-photon process. For nanoparticles with higher concentration

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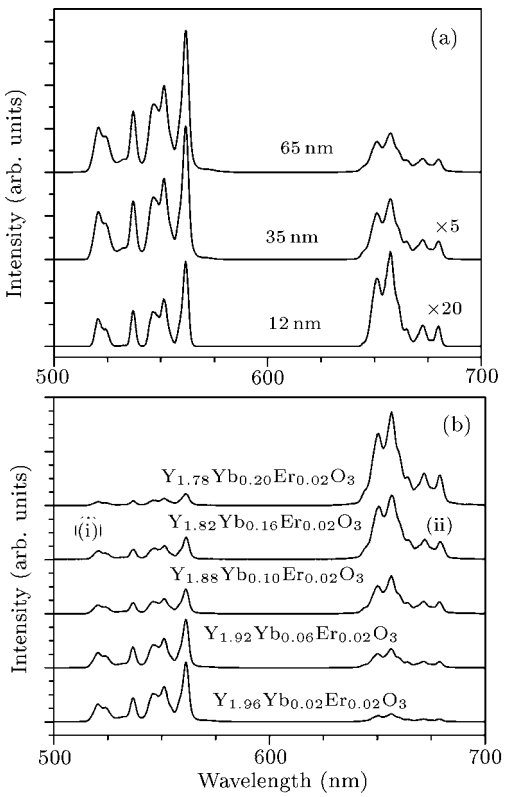

Fig. 1. (a) Upconversion luminescence spectra in Er^{3+} (1 mol%) and Yb^{3+} (3 mol%) codoped Y_2O_3 nanoparticles with different sizes. (b) Upconversion luminescence spectra in Er^{3+}/Yb^{3+} codoped 65-nm nanoparticles with different Yb^{3+} concentrations.

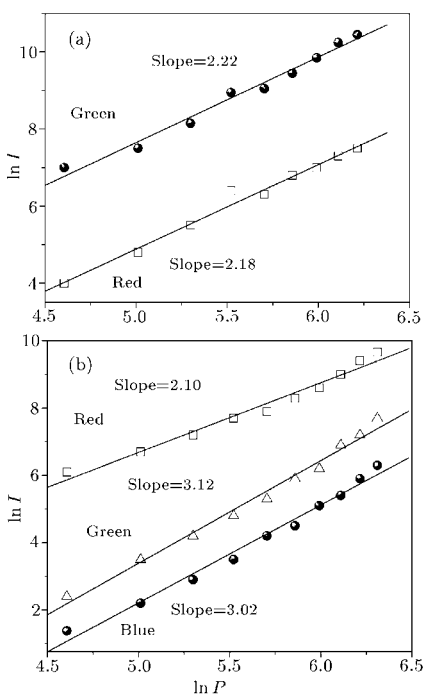

Fig. 2. The logarithm plots of the emission intensity I of the 65-nm (a) $Er_{0.02}Yb_{0.02}Y_{1.96}O_3$ and (b) $Er_{0.02}Yb_{0.20}Y_{1.78}O_3$ powders as a function of excitation power P.

of Yb^{3+}, the red emission yields a slope of ∼2, while the green as well as the blue emission of $^2H_{9/2}{-}^4I_{15/2}$ yields a slope of ∼3. This means that for the present nanoparticles, the population on the red level is a two-photon process, while the population of the green levels as well as the blue level is a three-photon process. Few author have observed three-photon population on the green levels in upconversion luminescence of Er/Yb co-activated materials although Song *et al.*[10] observed it in phosphate glasses.

Table 1. Variation of rise and decay time constants in nanoparticles with particle sizes.

Particle size (nm)	7	12	30	65
τ_1 (μs)		8	24	28
τ_2 (μs)	46	78	94	228

Table 2. Variation of the rise and decay time constants with Yb^{3+} concentration in the 65 nm samples.

Yb^{3+} concentration (mol%)		1	3	5	8	10
Green	τ_1 (μs)	17.8	9.8	9.1	8.8	3.0
	τ_2 (μs)	229	206	106	51	44
Red	τ_1 (μs)	5.5	6.8	4.0	5.8	4.0
	τ_2 (μs)	292	219	127	66	54

Figure 3 shows the upconversion luminescent dynamics measured in different time scales for the $^4S_{3/2}{-}^4I_{15/2}$ green transitions. As the time scale is in the range of 50 μs, only the rise process can be observed. In the range of 100–200 μs, both the rise and decay processes are observed. In the range of 1 ms, only the decay process is observed. In the figure, the luminescent dynamics is fitted with a universal function of

$$I(t) = I_0(e^{-t/\tau_2} - e^{-t/\tau_1}),$$

where τ_1 and τ_2 are the rise and decay time constants, respectively. If $t/\tau_2 \ll 1$, the function is simplified to an exponential growth: $I(t) = I_0(1 - e^{t/\tau_1})$. If $t/\tau_1 \gg 1$, it is simplified to an exponential decay: $I(t) = I_0 e^{-t/\tau_2}$. It should be noticed that the decay time constants measured in different time scales are different, indicating that at least two decay constants exist. In Fig. 3, τ_1 is determined to be 28 μs. while τ_2 is determined to be 228 μs. Figure 4 shows the luminescence dynamics measured in nanoparticles with different sizes. In Fig. 4(a), it is obvious that as the particle size decreases, the rise time constant becomes shorter. As the size decreases to several nanometres, the rise process nearly disappears. In Fig. 4(b), it can be observed that the decay time constant also decreases with the decreasing particle size. The variation of the rise time and decay time constants measured under the same conditions is listed in Table 1. Figure 5 shows the luminescence dynamics measured in nanoparticles with different Yb^{3+} concentrations for the green emission of $^4H_{11/2}{-}^4I_{15/2}$. It can be seen that as the Yb^{3+} concentration increases, both the rise and decay time constants decrease. The luminescence dynamics for the red emission at 15286 cm^{-1} is also investigated. The variation of the rise and decay time

constants with the Yb^{3+} concentration for the green and red emissions is listed in Table 2. Similar to the decay time constants for the green emission, the decay time constant for the red emission also decreases with the increasing Yb^{3+} concentration. Differing from the rise time constant for the green emission, the decay time constant for the red emission has little variation with the Yb^{3+} concentration. Compared to the green emission, the rise time constant for the red emission becomes shorter, while the decay time constant becomes longer.

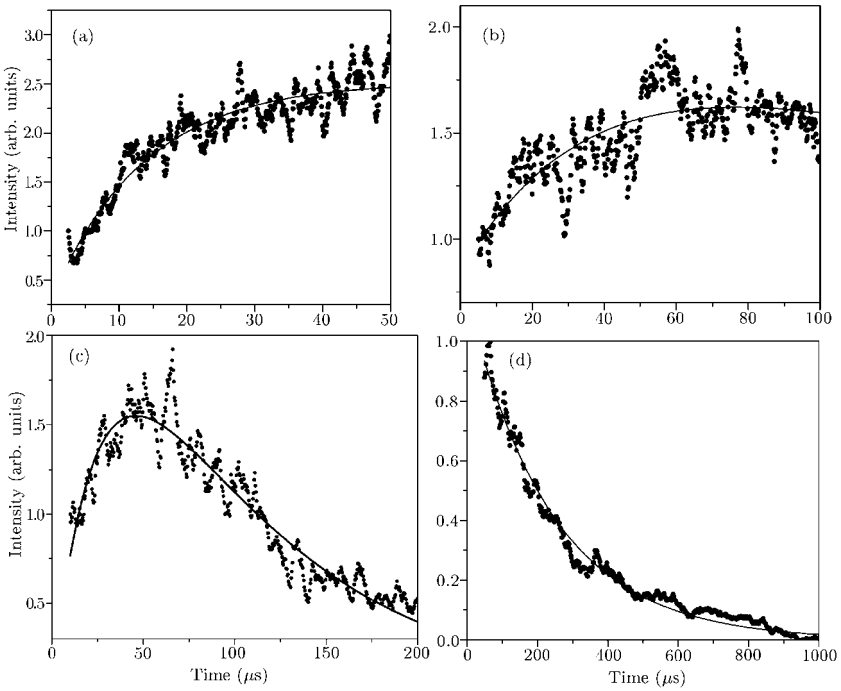

Fig. 3. Upconversion luminescent dynamics measured in different time scales (monitored at 18240 cm^{-1}).

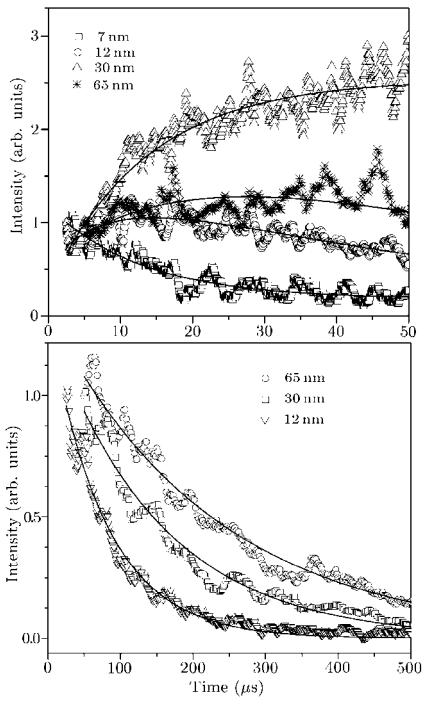

Fig. 4. Upconversion luminescent dynamics in nanoparticles with different sizes (monitored at 18240 cm^{-1}).

The up-conversion luminescence processes for Er^{3+} in Er/Yb-codoped nanocrystalline Y_2O_3 can be described in the following (see Fig. 6). Firstly, the Er^{3+} ion is excited from the ground state $^4I_{15/2}$ to the excited state $^4I_{11/2}$ by one of the three processes, i.e. the ground state absorption, the photon-assisted energy transfer (ET) from the Yb^{3+} $^2F_{5/2}$ level and the ET from the $^4I_{11/2}$ level of an adjacent Er^{3+} ion.[12] Among the three processes, the phonon-assisted ET from Yb^{3+} ion is the main one, since the Yb^{3+} ion has a absorption cross section larger than the Er^{3+} ion around 980 nm in the Y_2O_3 host. Secondly, the populated $^4I_{11/2}$ level is excited to the $^4F_{7/2}$ level by the same three processes, excited state absorption, phonon-assisted ET from the Yb^{3+} ion and ET from an adjacent Er^{3+} ion. The populated $^4F_{7/2}$ may mostly nonradiatively relax to two lower levels: $^2H_{11/2}$ and $^4S_{3/2}$, which produce two green upconversion emissions. On the other hand, the Er^{3+} ion populated $^4I_{11/2}$ level mostly relaxes nonradiatively to the long-living $^4I_{13/2}$ level. The populated $^4I_{13/2}$ level may be excited to the $^4F_{9/2}$ level by the same three processes. The populated $^4F_{9/2}$ level of the Er^{3+} ion most relaxes radiatively to the ground state $^4I_{15/2}$ level, which causes red emissions. It may be excited to the $^2H_{9/2}$ level by the third photon by the same three processes, produce weak blue emission.[11] The electrons of $^2H_{9/2}$ may also relax to $^2H_{11/2}/^4S_{3/2}$ to produce the three-photon green emission.

As the particle size decreases, a great number of surface defects are involved, which act as nonradiative transition channels.[13,14] Capobianco *et al.*[15] observed that the nanocrystalline lattice of Y_2O_3 contains CO_3^{2-} and OH^- impurities on their surface and thus have available large vibrational modes to efficiently depopulate the excited states nonradiatively. Thus, the nonradiative relaxation rates become much greater, leading to the decreasing emission intensity. At the same time, the increase of $^4I_{11}$–$^4I_{13}$ nonradiative relaxations leads population of $^4F_{9/2}$ and the red-emission intensity to increase relatively. As the Yb^{3+} concentration increases, the ET excitation for Er^{3+} becomes effective, leading to the increasing intensity of the red emissions. However, due to the ET of $^4H_{11/2}(Er) + {}^2F_{7/2}(Yb^{3+}) \rightarrow {}^4I_{13/2}(Er^{3+}) + {}^2F_{7/2}(Yb^{3+})$, the green-emission intensity decreases.[7]

Now let us consider the size-dependent luminescence dynamics. In Y_2O_3 nanoparticles prepared by combustion, nonradiative transition rate increases

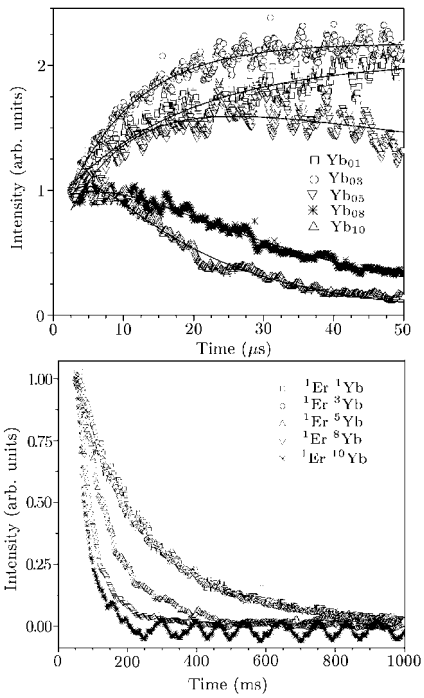

Fig. 5. Upconversion luminescent dynamics in nanoparticles (65 nm) with different Yb^{3+} concentrations (monitored at 18240 cm^{-1}).

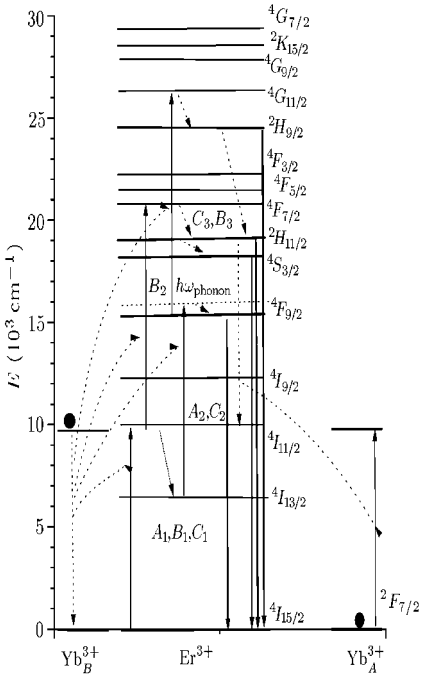

Fig. 6. A schematic diagram of upconversion luminescence processes for Er^{3+}/Yb^{3+} codoped nanocrystalline yttria. *A*, *B* and *C* represent the population processes for the red, green and blue levels, respectively.

greatly with the decreasing particle size. The nonradiative transition rate for Yb^{3+} in the excited state $^2F_{7/2}$ should also increase with the decreasing particle size. Under the excitation of the pulsed laser with duration of 10 ns, which is much shorter than the population lifetime of *f* states, the rise time constant in upconversion dynamics of Er^{3+} is actually dominated by the excited lifetime of $^2F_{7/2}$ for Yb^{3+}. The reverse of lifetime for Yb^{3+} equals to the sum of radiative and nonradiative transition rate *W* for $^2F_{7/2}$ of Yb^{3+} and the total energy transfer rate *X* from Yb^{3+} to Er^{3+}. Assuming that the energy transfer rate and radiative transition rate of Yb^{3+} has only a little variation with particle size, then we can deduce that the rise time constant decreases with the decreasing particle size. If *W* is much larger than *X*, the ET of $^4I_{11/2}(Er^{3+}) + {}^2F_{7/2}\ (Yb^{3+}) \rightarrow {}^4S_{3/2}(Er^{3+}) + {}^2F_{7/2}(Yb^{3+})$ and $^4I_{13/2}(Er^{3+}) + {}^2F_{7/2}\ (Yb^{3+}) \rightarrow {}^4F_{9/2}(Er^{3+}) + {}^2F_{7/2}(Yb^{3+})$ is ineffective. In the case of the ESA of Er^{3+} dominated the upconversion luminescence for the red and green emissions, the rise process is much shorter than several ten μs.

In conclusion, we have investigated the unconversion luminescence and dynamics for Er^{3+}/Yb^{3+} codoped Y_2O_3 nanocrystals. It is found that as the particle size decreases, the upconversion luminescence intensity decreases greatly due to the increase of nonradiative transition rate for both Er^{3+} and Yb^{3+}. At the same time, the rise and the decay time constants become shorter. As the particle size decreases to several nanometres, the ET of $Yb^{3+} \rightarrow Er^{3+}$ becomes ineffective, nearly leading to the disappearance of the rise process. The population on the red level $^4F_{9/2}$ is always a two-photon process. The population on the green levels $^2H_{11/2}$ and $^2S_{3/2}$ depends on the concentration of Yb^{3+}. As the concentration of Yb^{3+} is lower, it is a two-photon process. As the concentration of Yb^{3+} is higher, it is a three-photon process. A detailed upconversion luminescence process under 980-nm pulsed laser excitation has been provided.

References

[1] Matsuura D 2002 *Appl. Phys. Lett.* **81** 4526
[2] Capobianco J A et al 2002 *J. Phys. Chem.* B **106** 1181
[3] Vetrone F et al 2003 *J. Phys. Chem.* B **107** 1107
[4] Hebert T et al 1990 *Appl. Phys. Lett.* **57** 1727
[5] Mita Y et al 1993 *J. Appl. Phys.* **74** 4703
[6] Downing E, Hesselink L, Ralston J and Macfarlane R 1996 *Science* **273** 1185
[7] Di Paolo R E et al 2001 *J. Phys. Condens. Matter* **13** 7999
[8] Pollnau M et al 2000 *Phys. Rev.* B. **61** 3337
[9] Chamarro M A and Cases R 1990 *J. Lumin.* **46** 59
[10] Song F, Zhang G, Shang M and Tan H, Yang J and Meng F 2001 *Appl. Phys. Lett.* **79** 1748
[11] Song H et al 2004 *Solid State Commun.* **132** 409
[12] Huang J, Xue S, Yang B, Liu S and Shen J 1997 *Appl. Phys. Lett.* **70** 2335
[13] Song H, Wang J, Chen B and Lu S 2003 *Chem. Phys. Lett.* **376** 1
[14] Peng H, Song H, Chen B, Wang J, Lu S and Kong X 2003 *J. Chem. Phys.* **118** 3277
[15] Capobianco J A, Vetrone F, Alesio T, Tessari G, Bettinelli A and Bettinelli M 2000 *Phys. Chem. Chem. Phys.* **2** 3203