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Energy transfer to enhance the characteristics emission from lanthanide-doped nanocrystals

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Abstract. We report the improved characteristic emission of Er^{3+} ions by co-doping wide-band-gap SnO_2 nanocrystals (NCs), which as sensitizers of Er^{3+} ions. It is found that the Er^{3+}-related near infrared emission is enhanced by three orders of magnitude, which can be attributed to the effective energy transfer process occurs between SnO_2 nanocrystals and Er^{3+} ions. Meanwhile, we also prepare the Er^{3+}-Yb^{3+} co-doped $NaYF_4$ NCs with Gd^{3+} dopant ions to obtain high-efficiency up-conversion emission by energy transfer from Yb^{3+} to Er^{3+}. We demonstrate experimentally that Gd^{3+} dopant ions play key roles in the formation of β-$NaYF_4$ NCs which can improve the energy transfer efficiency from Yb^{3+} to Er^{3+} obviously. Consequently, the up-conversion emission is enhanced by more than five times.

1. Introduction

Recently, the studies on down- and up-conversion process in Lanthanide-doped nanomaterials have attracted much attention since it can be used to improve the performance of many kinds of optoelectronic devices [1,2]. However, due to small absorption cross sections and small radiative decay rates of trivalent lanthanide ions, the emission efficiency in lanthanide-doped nanomaterials is still low, which prevents their practical applications. To increase the absorption of Lanthanide-doped doped nanocrystals (NCs), the host materials are often additionally doped with strongly absorbing ions (Yb^{3+}) or wider band gap materials (ZnO NCs, In_2O_3 NCs) called sensitizers, which should also ensure efficient energy transfer to the activator.

In our previous work, the near-infrared (1.54 um) emission intensity of Er^{3+} ions under 325nm excitation was enhanced by 100 times by co-doping 3 nm In_2O_3 NCs as sensitizers[3]. Here, we report the improved down-shift emission of Er^{3+} ions by co-doping wide-band-gap SnO_2 NCs, which as sensitizers of Er^{3+} ions[4]. Meanwhile, we also prepare the Er^{3+}-Yb^{3+} co-doped $NaYF_4$ NCs with Gd^{3+} dopant ions to obtain high-efficiency up-conversion emission by energy transfer from Yb^{3+} to Er^{3+}. We demonstrate experimentally that Gd^{3+} dopant ions play key roles in the formation of β-$NaYF_4$ NCs which can improve the energy transfer efficiency from Yb^{3+} to Er^{3+} obviously.

2. Experimental

A sol-gel process was used to fabricate the SiO_2 thin films co-doped with Er^{3+} ions and SnO_2 NCs, as we previously reported[4].The $NaYF_4$:Yb,Er NCs were synthesized by a hydrothermal method. Briefly, 1.5 g NaOH was dis-solved in 7.5 mL deionized water, then mixed with 25 mL of ethanol and 25 mL of oleic acid under stirring. 10 mL 0.2 M $RE(NO_3)_3$ and 5 mL 2 M NH_4F were added to the resulting mixture. The solution was transferred into a 100 mL of Teflon-lined autoclave and heated at 180℃ for 2 h. The NCs were washed with water and ethanol several times and collected by centrifugation.

Finally, the NCs were dry at 60℃ for 12 h and re-dispersed into ethanol to form an aqueous dispersion and were ready for use.

3. Results and discussion

The amount of Er^{3+} ions added into SiO_2 thin films was fixed at 5% (molar ratio). The SnO_2 NCs are about 4-6 nm as shown in inset of figure 1. Figure 1 shows the photoluminescence (PL) spectra of the SiO_2 thin films doped with SnO_2 NCs and Er^{3+} ions. Sn-free and 20% Sn films show the same peak at 1540 nm under laser excitation at 325 nm. After co-doping of SnO_2 NCs, the down-shift emission of 20% Sn sample is more than three orders of magnitude to the Sn-free sample due to the energy transfer process occurs between SnO_2 NCs and Er^{3+} ions. The wider band gap SnO_2 NCs have large absorption cross-sections to incident UV-light and can effectively improve the density of sensitizing Er^{3+} ions, then improve the characteristic emission of Er^{3+} ions.

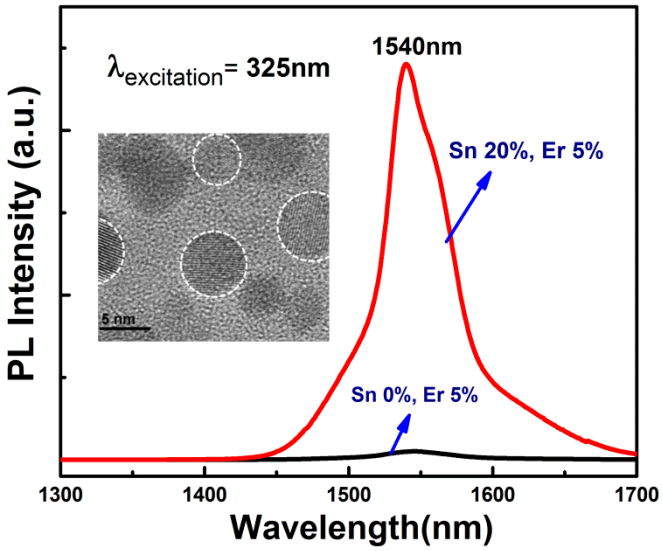

Figure 1. PL intensities at 1540 nm for 5 mol% Er^{3+} ions and 20 mol% Sn co-doped silica films excited at 325 nm (black line, multiplied by a factor of 1000 to allow the comparison); inset is high-resolution TEM image of SnO_2 NCs doped in SiO_2 thin films.

Figure 2(a) shows up-conversion PL intensities of $NaYF_4$:Yb,Er NCs for Gd0 (0 mol% Gd^{3+} doped ions) and Gd15 (15 mol% Gd^{3+} doped ions) samples excited at 980 nm with a laser power of 656 mW. The electron of Yb^{3+} is excited at 980 nm in $NaYF_4$:Yb,Er NCs and then it can transfer the energy to the Er^{3+}. As shown in Figure 2(a), there are three major emission bands at 521nm (green light), 539 nm (green light), and 654 nm (red light), which are assigned to the $^2H_{11/2}$ to $^4I1_{5/2}$, $^4S_{3/2}$ to $^4I_{15/2}$, and $^4F_{9/2}$ to $^4I1_{5/2}$ transitions of Er^{3+} ions, respectively. Figure 2(a) shows the up-conversion luminescence intensities of Gd15 sample clearly stronger than Gd0 sample due to a small residual amount of β-$NaYF_4$ phase appearing, as a well consistent with the presence of two phases observed by XRD in Figure 2(b). As shown in Figure 2(b), the diffraction peaks of the Gd0 sample agree well with those calculated for the α-$NaYF_4$ phase (JCPDS card, No.77-2042). However, there was a small residual amount of β-$NaYF_4$ phase (JCPDS card, No.16-0334) of Gd15 sample. In Figure 2(b) inset TEM images, we can see a few larger $NaYF_4$ rods of Gd15 sample, which confirm β-$NaYF_4$ phase is formed. And we see no rods in Gd0 sample. We conclude that Gd^{3+} dopant ions play key roles in the formation of β-$NaYF_4$ NCs. It can be partly attributed to the crystal structure of β-$NaYF_4$ phase consists of an ordered array of F^{2-} ions with two types of relatively low-symmetry cation sites selectively occupied by Na^+ and RE^{3+} ions, resulting in significant electron cloud distortion of the cations to accommodate the structural change. Importantly, light lanthanides with large ionic radii (Gd^{3+}) exhibit a high tendency towards electron cloud distortion owing to increased dipole polarizability, and thus favour

the hexagonal structures[5]. The Gd^{3+} ions induce phase changed which may improve the energy transfer efficiency from Yb^{3+} to Er^{3+}, then improve the up-conversion emission.

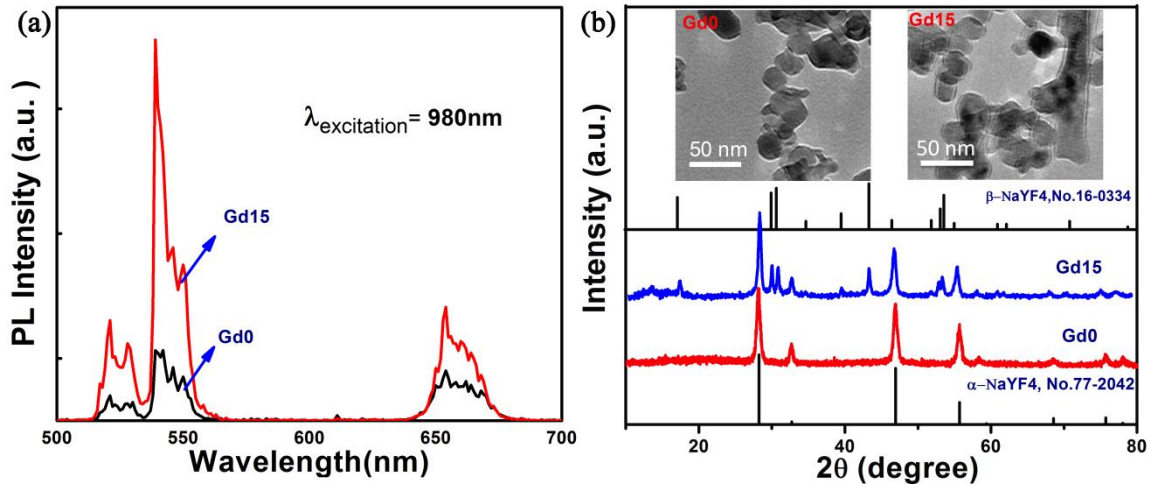

Figure 2. (a) up-conversion PL intensities of $NaYF_4$:Yb,Er NCs for Gd0 and Gd15 samples excited at 980 nm with a laser power of 656 mW; (b) XRD patterns of $NaYF_4$:Yb,Er NCs for Gd0 and Gd15 samples, insets are TEM images of Gd0 and Gd15 samples.

4. Conclusions

We have fabricated SiO_2 thin films co-doped with Er^{3+} ions and SnO_2 NCs. We find that the Er^{3+}-related down-shift emission is enhanced by three orders of magnitude due to the effective energy transfer process occurs between SnO_2 NCs and Er^{3+} ions. Furthermore, we also have prepared the Er^{3+}-Yb^{3+} co-doped $NaYF_4$ NCs with Gd^{3+} dopant ions to obtain high-efficiency up-conversion emission by energy transfer from Yb^{3+} to Er^{3+}. We demonstrate experimentally the up-conversion emission of $NaYF_4$:Yb,Er NCs with Gd^{3+} dopant ions is enhanced by more than five times. We conclude that Gd^{3+} ions play key roles in the formation of β-$NaYF_4$ NCs which can improve the energy transfer efficiency from Yb^{3+} to Er^{3+} obviously. The present work provides a novel approach to enhance the characteristics emission from lanthanide-doped nanomaterials, which indicates the possibility to improve the down- and up-conversion efficiency for device applications.

5. Acknowledgments

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6. References

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