Study on Upconversion Properties of $NaYF_4$:Er Nanocrystals by Off-Resonant Excitation

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1. Introduction

Upconversion (UC) materials have attracted significant attention because of their potential applications to solar cells, telecommunications, biolabeling, 3-dimensional displays and temperature sensing. Lanthanide ion doped $NaYF_4$ is one of the promising materials for UC, since the phonon energy of the host is relatively low which suppresses non-radiative relaxation. There have been several reports regarding the UC properties of $NaYF_4$:Er, in which the excitation energy corresponds to the energy of the lowest f-f transition of Er^{3+} ($^4I_{15/2}\rightarrow{}^4I_{13/2}$), that is, resonant excitation, however, the UC properties of off-resonant excitation is not so well understood. In this work, we studied the UC optical process in the hexagonal phase of $NaYF_4$:10%Er^{3+}/$NaYF_4$ core/shell nanocrystals (NCs) using off-resonant excitation with the wavelength of 1620 nm. Absorption spectrum, Raman spectrum and the temperature and power dependence of the UC emission were measured, and the UC optical process is discussed.

2. Experimental Approach and Results

The hexagonal phase of $NaYF_4$:10%Er^{3+} nanocrystals were synthesized using $Y_2(CO_3)_3\cdot xH_2O$, $Er_2(CO_3)_3\cdot xH_2O$, Na_2CO_3 and NH_4F with oleic acid and octadecene. To produce core/shell NCs, the synthesized $NaYF_4$:10%Er^{3+} NCs were mixed with $Y_2(CO_3)_3\cdot xH_2O$, Na_2CO_3, and NH_4F solved in OA and ODE. The prepared NCs powder was characterized by X-ray diffraction and transmission electron microscope. UC emission spectra were measured using 1620 and 1550 nm laser as excitation source for off-resonant and resonant excitation, respectively.

The XRD data demonstrates that pure β-phase $NaYF_4$:Er nanocrystal have been fabricated. The up-conversion emission spectra under resonant excitation condition are dominated by four peaks at around 980nm ($^4I_{11/2}\rightarrow{}^4I_{15/2}$), 800nm ($^4I_{9/2}\rightarrow{}^4I_{15/2}$), 660nm ($^4F_{9/2}\rightarrow{}^4I_{15/2}$) and 540nm ($^4S_{3/2}\rightarrow{}^4I_{15/2}$). The excitation power dependence of UC was plotted by a double-logarithmic representation. The values of the slope n were n=1.62, n=1.73 (2-step UC) and the n=2.31, n=2.21 (3-step UC) for 980nm, 800nm emission and 660nm, 540nm emission, respectively. Similar UC emission spectra were obtained by off-resonant excitation, however, high density excitation is necessary to get similar UC emission intensity under resonant excitation.

To investigate the cause of the off-resonant excitation, optical absorption and Raman spectra were measured. Two absorption peaks were observed at 1523 and 1599 nm, the former of which can be assigned to the $^4I_{15/2}\rightarrow{}^4I_{13/2}$ transition of Er^{3+}. The energy difference between the two peaks is about 315 cm^{-1}, which is roughly the same as the phonon energy of the $NaYF_4$ as measured by Raman spectra. Therefore, the absorption peak at 1599 nm can be assigned as lattice vibrational absorption. In the UC measurements, the energy difference between off-resonant and resonant excitations is 280cm^{-1}, which roughly corresponds to the lattice vibration energy. Therefore, UC emission by off-resonant excitation is caused by phonon assisted excitation.

There are some optical processes for UC, that is, energy transfer upconversion, excited state absorption, cooperative excitation and so on, and the highest probable process is believed to be energy transfer excitation. The optical process for UC in $NaYF_4$:Er was studied using resonant and off-resonant excitation.

Fig. 1 shows the UC emission spectra of $NaYF_4$:Er^{3+}/$NaYF_4$ NCs under 1550, 1620 nm and two–color excitation with the excitation density of 160 mW/cm^2 at 80 K. The UC emission intensity for off-resonant excitation was almost zero, however, about 20 % UC enhancement was obtained under two-color excitation, compared to the UC intensity only under 1550 nm excitation. These results indicate that the UC probability through the excited state absorption is about one order of magnitude less than that of the energy transfer.

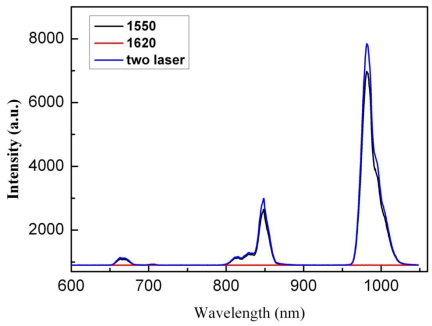

Fig. 1 *UC emission spectra of $NaYF_4$:10%Er^{3+}/$NaYF_4$ NCs under 1550, 1620 nm and two–color excitation with the excitation density of 160 mW/cm^2 at 80 K.*

3. Conclusions

UC optical process in the hexagonal phase of $NaYF_4$:10%Er^{3+}/$NaYF_4$ core/shell nanocrystals (NCs) using resonant and off-resonant excitation with the wavelength of 1550nm and 1620 nm, respectively, has been studied. It was found that the off-resonant UC is enhanced by phonon assisted excitation and that the contribution of the excited state absorption process to the UC is relatively high compared with that believed so far.