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New approach to enhance the up-conversion efficiency in the Ho^{3+}-Yb^{3+} co-doped system*

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We investigate the up-conversion luminescence spectra of Ho^{3+}-Yb^{3+} co-doped materials excited with two types of laser. It is found that the efficiency of green emission ($^5S_2$–$^5I_8$) can be enhanced by restraining the transition of $^5S_2$–$^5I_7$ since the two types of radiation both start on the $^5S_2$ level. We propose an important approach to enhance an expected up-conversion emission.

Keywords: energy up-conversion, Ho^{3+}-Yb^{3+} co-doped, energy transfer
PACC: 7820, 7855, 7860

1. Introduction

In the past thirty years, the up-conversion luminescence of some rare-earth ions doped in suitable host materials has been widely investigated.[1–9] However, there is still the urgent task of enhancing their up-conversion efficiencies which determine the prospects of their practical application. Although abundant levels of rare-earth ions provide multitudinous up-conversion pathways, the unexpected emission channels of a certain level result in energy loss and decrease the expected luminescence efficiency. Ho^{3+} is a well-investigated rare-earth ion for up-conversion processes. Early in 1990, continuous wave (CW) tunable green laser emission between 540 and 553 nm was achieved in Ho^{3+}-doped fluorozirconate fibres.[4] However, strong red emission of $^5S_2$–$^5I_7$ occurs in company with the green radiation of $^5S_2$–$^5I_8$ when pumped with a 647.1 nm red laser. It is reasonable to deduce that, if the $^5S_2$–$^5I_7$ transition is effectively restrained by an appropriate approach, the efficiency of the $^5S_2$–$^5I_8$ emission can be enhanced. This project can be realized by selecting a suitable excitation source. When excited with a 930 nm diode laser, strong green emission has been observed while the red emission of $^5S_2$–$^5I_7$ becomes very weak in the Ho^{3+}-Yb^{3+} co-doped sample. It is found that Yb^{3+} ions not only realize the population of $^5S_2$ by energy transfer but also restrain the radiation transition of $^5S_2$–$^5I_7$ by enhancing the population of $^5I_7$. We propose a new way to improve the efficiency of the green emission of $^5S_2$–$^5I_8$ of Ho^{3+}.

2. Experiment and results

In order to attain a relatively low phonon energy of the host and thus reduce multi-phonon emission of rare-earth ions, some fluoride compounds with low vibration frequency[8] are chosen as the original components of the host. The original compositions of the sample are $46CdF_2$–$24PbF_2$–$20BaF_2$–$3AlF_3$–$4NaF$–$2Yb_2O_3$–$1Ho_2O_3$. Having been ground thoroughly, the mixture was heated to 900°C and kept at that temperature for 15 min. Finally the sample was obtained by pouring the melt into a copper crucible. The up-conversion spectra were measured with a Japan R-500 spectrometer and two types of excitation source were adopted: a 632.8 nm He–Ne laser and a 930 nm light diode. Figures 1 and 2 show the up-conversion spectra pumped with 632.8 and 930 nm light respectively. The relative intensities of all observed up-conversion emissions excited with 930 and 632.8 nm wavelengths are listed in Table 1.

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Table 1. Relative intensities of up-conversion emission excited with 930 and 632.8 nm.

Up-converted emission		$^5F_3$–$^5I_8$ (485 nm)	$^5S_2$–$^5I_8$ (540 nm)	$^5S_2$–$^5I_7$ (740 nm)	$^5F_5$–$^5I_8$ (658 nm)
Relative intensity	Excited with 632.8 nm	0.3	11	100	
	Excited with 930 nm	–	100	0.2	22.6

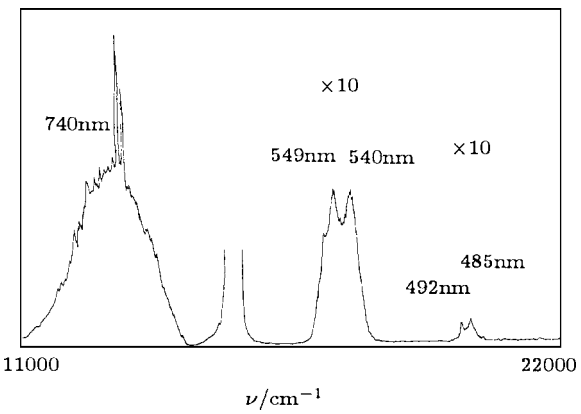


Fig.1. Up-converted emission spectra with excitation of 632.8 nm He–Ne laser.

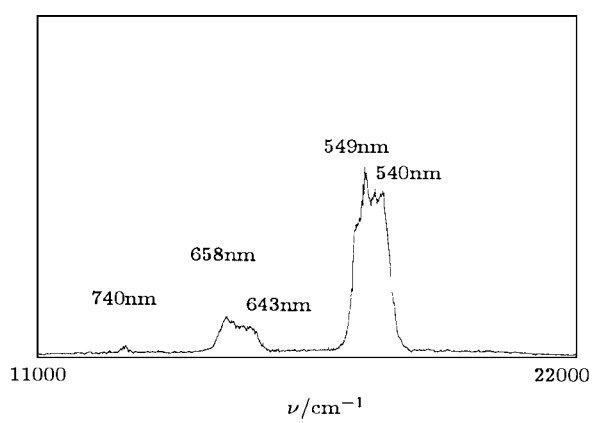


Fig.2. Up-converted emission spectra with excitation of 930 nm diode light.

The up-conversion spectra pumped at 930 nm are obviously different from those pumped at 632.8 nm. The ratio of emission at 740 nm to that at 540 nm is 9.09 when excited with a 632.8 nm laser. When pumped with a 930 nm diode light, the green luminescence is much stronger than other emissions. It seems that the up-conversion emissions are concentrated on the $^5S_2$–$^5I_8$ transition in the visible region. The spectral difference indicates that the 540 nm emission is drastically restrained by the $^5S_2$–$^5I_7$ transition, considering that both 740 and 540 nm are emitted by the $^5S_2$ level.

3. Discussion

In order to discuss the up-conversion mechanism in a Ho^{3+}-Yb^{3+} co-doped system with an excitation of 930 nm, a two-step sensitization process[11] may be adopted. According to this model, the Yb^{3+} ion in $^2F_{5/2}$ transfers its energy to Ho^{3+} and populates the $^5I_6$ level of Ho^{3+}. The population of $^5S_2$ of Ho^{3+} can be realized by excited state absorption of Ho^{3+} or a second energy transfer between Yb^{3+} and Ho^{3+}. Both the non-radiative emission of $^5I_6$ and the radiation transition of $^5I_6$–$^5I_7$ can populate the $^5I_7$ level. Non-radiative decay from $^5S_2$ also results in the population of $^5F_5$. The 658 nm emission from $^5F_5$ to $^5I_8$ is weak due to the relatively low phonon energy of the host. These processes are depicted in Fig.3.

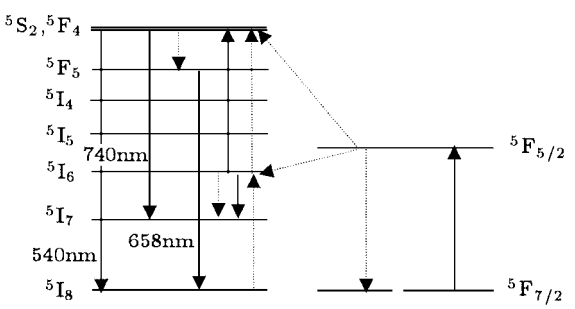


Fig.3. Level diagram and up-conversion mechanism in a Ho^{3+}-Yb^{3+} co-doped system pumped at 930 nm.

In order to discuss the decreased 740 nm emission ($^5S_2$–$^5I_7$), a simplified three-level system is used to analyse the up-converting dynamical behaviour. The equations for the population densities can be expressed as

$$\frac{dn_3}{dt} = \beta N_2 n_2 - W_{31} n_3 - W_{32} n_3 + R n_2, \quad (1)$$

$$\frac{dn_2}{dt} = W_{32} n_3 - W_{21} n_2 + \alpha N_2 n_1 - \beta N_2 n_2 - R n_2, \quad (2)$$

$$\frac{dn_1}{dt} = W_{31} n_3 + W_{21} n_2 - \alpha n_1 N_2, \quad (3)$$

$$\frac{dN_1}{dt} = -P N_1 + W N_2 + \alpha n_1 N_2 + \beta n_2 N_2, \quad (4)$$

$$\frac{\mathrm{d}N_2}{\mathrm{d}t} = PN_1 - WN_2 - \alpha n_1 N_2 - \beta n_2 N_2, \quad (5)$$

$$n_1 + n_2 + n_3 = n, \quad (6)$$

$$N_1 + N_2 = N. \quad (7)$$

Here n_1 and n_3 denote the population densities in levels $^5\mathrm{I}_8$ and $^5\mathrm{S}_2$, respectively; $^5\mathrm{I}_6$ and $^5\mathrm{I}_7$ are assumed to be one level, marked n_2; R is the pumping rate from n_2 to n_3 levels; W_{ij} is the radiation transition rate from i to j; N_2 is the concentration of Yb^{3+} ions in their excited state; α and β are the energy transfer rates of $^2\mathrm{F}_{5/2}(\mathrm{Yb}^{3+})$ to $^5\mathrm{I}_6(\mathrm{Ho}^{3+})$ and $^2\mathrm{F}_{5/2}(\mathrm{Yb}^{3+})$ to $^5\mathrm{S}_2(\mathrm{Ho}^{3+})$, respectively.

Thus under the steady-state condition, the relation of emission rates W_{31} and W_{32} with the population densities of n_2 and n_1 can be expressed as

$$\frac{W_{32}}{W_{31}} = \frac{\alpha N_2 n_1 - (2\beta N_2 + R + W_{21})n_2}{W_{21}n_2 - \alpha N_2 n_1}. \quad (8)$$

The ratio of emission intensity of 740 to 540 nm can be described by the following equation

$$\frac{I_{32}}{I_{31}} = \frac{n_3 h\gamma_{32} W_{32}}{n_3 h\gamma_{31} W_{31}} \approx 1.37\frac{\alpha N_2 - (2\beta N_2 + R + W_{21})\eta}{W_{21}\eta - \alpha N_2}, \quad (9)$$

where $\eta = n_2/n_1$.

It is evident, from Eq.(6), that the value of I_{32}/I_{31} decreases as the electronic population ratio of n_2 to n_1 increases. When η is close to $\alpha N_2/(2\beta N_2 + R + W_{21})$, the value of I_{32}/I_{31} nearly equals zero, indicating that the transition from n_3 to n_2 almost disappears. Thus, this means that the red emission of $^5\mathrm{S}_2$–$^5\mathrm{I}_7$ can be effectively restrained by populating its terminated level $^5\mathrm{I}_7$ if a suitable host is found and an appropriate pumping source is adopted.

4. Conclusion

For a certain level of a rare-earth ion with multiple emission channels, the unexpected emission can be restrained by populating its terminated level of the emission channel, and accordingly the luminescence efficiency we expect is enhanced. Thus a new project to enhance up-conversion efficiency has been proposed. The project can also be applied to investigate Er^{3+} or Yb^{3+}-Er^{3+} co-doped up-conversion materials in respect of the fact that the transition of $^2\mathrm{S}_{3/2}$ to $^4\mathrm{I}_{13/2}$ can also reduce the efficiency of the green emission of $^2\mathrm{S}_{3/2}$ to the ground. But the available approach should be further explored.

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