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Co-precipitation synthesis and upconversion luminescence properties of ZrO_2:Yb^{3+}-Ho^{3+}

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Abstract. ZrO_2:Yb^{3+}-Ho^{3+} **phosphors with different** Yb^{3+} **doping concentration have been prepared by co-precipitation method. X-ray diffraction (XRD), scanning electron microscope (SEM) and photoluminescence spectra were used to characterize the properties of** ZrO_2:Yb^{3+}-Ho^{3+} **phosphors. Different phases of** ZrO_2 **can be obtained by changing the concentration of** Yb^{3+}. **Under the 980 nm excitation, the sample gives a set of light: strong green (539 nm), weak red (670 nm) and near-infrared (760 nm). The upconversion luminescence is based on two-photon absorption by the energy transfer from the donor (**Yb^{3+}**) to the acceptor (**Ho^{3+}**). All the results indicate that** ZrO_2:Yb^{3+}-Ho^{3+} **phosphors could be a promising biological labelling material.**

Keywords. ZrO_2; phosphor; co-precipitation; upconversion.

1. Introduction

Researches of rare-earth-doped upconversion (UC) materials as fluorescent labels, temperature-sensing probes, solid-state lasers and new generation television screens have recently started to be considered[1,2] due to their enhanced luminescent properties induced by the small size. UC process is the generation of visible or UV light from lower energy radiation (usually near-infrared radiation), through the use of lanthanide, such as Er^{3+}, Tm^{3+} and Ho^{3+}, doped into a solid-state host.[3] The use of Yb^{3+} as sensitizer of Ho^{3+} is an option due to efficient energy transfer between Yb^{3+} and Ho^{3+} and the existence of commercially available diode lasers operating around 980 nm suitable for pumping Yb^{3+} ions.[4] Recently, oxide nanocrystals as UC hosts have been intensively investigated due to good chemical stability.[5] Especially, ZrO_2 host can be used in a variety of photonics and industrial applications due to low phonon energy (470 cm^{-1}), superior hardness, high refractive index, optical transparency and chemical stability.[6,7]

Considerable amount of work has been reported on the mechanical and other physical properties of ZrO_2:Yb^{3+}-Ln^{3+} (Ln^{3+} = Er^{3+}, Tm^{3+}),[8,9] whereas only few research works have been done on the luminescence properties of ZrO_2:Yb^{3+}-Ho^{3+}. Solís *et al*[10] and Rosa *et al*[11] have prepared ZrO_2:Yb^{3+}-Ho^{3+} by sol–gel method and studied their structural and UC emission properties. Co-precipitation is one of the most promising techniques because air-stable and moisture-stable precursor powders can be prepared on a large scale in water rather than in organic chemicals. However to our knowledge, no paper about ZrO_2:Yb^{3+}-Ho^{3+} prepared

by co-precipitation has been reported. In this work, the UC luminescence properties of the ZrO_2:Yb^{3+}-Ho^{3+} nanocrystals as a function of the Yb^{3+} content are investigated. With the increase of Yb^{3+} concentration, the samples transit from monoclinic to cubic phase. Explanations for this UC luminescence behaviour are presented and discussed via the variation of excitation power at 980 nm.

2. Experimental

The powder samples of ZrO_2:Yb^{3+} (1–16 mol%)-Ho^{3+} (fixed 1 mol%) have been synthesized using a homogeneous co-precipitation method. $ZrOCl_2 \cdot 8H_2O$ (AR), Yb_2O_3 (99.99%), $Ho_2O_3 \cdot 6H_2O$ (99.99%) and ammonium hydroxide were prepared for the starting materials without further purification. A procedure for the sample synthesis of ZrO_2:Yb^{3+}-Ho^{3+} is typically described as follows: Yb_2O_3 and Ho_2O_3 were dissolved in dilute nitric acid under heating. After the Yb_2O_3 and Ho_2O_3 were completely dissolved, the excess nitrite acid was removed at high temperature. Then de-ionized water was added to obtain $Yb(NO_3)_3$ and $Ho(NO_3)_3$ solutions. Subsequently, certain amount of $ZrOCl_2 \cdot 8H_2O$, $Yb(NO_3)_3$ and $Ho(NO_3)_3$ were dissolved in de-ionized water. The mixture was stirred for 0.5 h to obtain a homogeneous solution. Then the white precipitate was formed by slowly dropped ammonium hydroxide with magnetic stirring. The precipitate was filtrated and washed twice with de-ionized water. The precipitate was dried at 80°C in oven for 10 h. In the end, the precipitate was grinded and annealed at 850°C for 3 h in air to obtain the white phosphor sample. The other phosphors of ZrO_2:Yb^{3+}-Ho^{3+} with different Yb^{3+}-doped concentration were synthesized by the same procedure with the corresponding amount of raw materials.

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The samples were characterized by powder X-ray diffraction (XRD) performed on a Panalytical X' Pert diffractometer using CuKa$_1$ radiation ($\lambda = 0.154187$ nm). The morphology patterns of samples were obtained on a field emission scanning electron microscope (SEM JSM6700F) equipped with an energy-dispersive X-ray spectrum (EDS). The UC luminescence spectra excited with a mode-locked picosecond Ti:Sapphire laser (Tsunami, Spectra Physics) at 980 nm were detected with PMT detector (R928). Raman spectra were obtained on a Jobin-Yvon HR800 Laser Raman Microscope under 488 nm laser excitation. All measurements were carried out at room temperature.

3. Results and discussion

3.1 *Structure, morphology and composition of ZrO$_2$:Yb^{3+}-Ho^{3+}*

The XRD patterns of ZrO$_2$:Yb^{3+}-Ho^{3+} for different concentration of Yb^{3+} co-doped with 1 mol% of Ho^{3+} in comparison with the standard cards are shown in figure 1. It can be seen clearly from figure 1 that, with the increase of Yb^{3+} doping concentration, the phase of ZrO$_2$:Yb^{3+}-Ho^{3+} samples convert from the mixed phase to the pure cubic phase. All diffraction peaks in XRD curve of ZrO$_2$:1 mol% Yb^{3+}-1 mol% Ho^{3+} are indexed to mixed phase, namely, in good agreement with the standard data of monoclinic ZrO$_2$ (Joint

Figure 1. XRD patterns of ZrO$_2$:Yb^{3+}-Ho^{3+} nanocrystals for different concentrations (1, 2, 4, 8, 12 and 16 mol%) of Yb^{3+} co-doped with 1 mol% of Ho^{3+}.

Committee for Power Diffractions Standards, JCPDS card no. 78-0047) and cubic ZrO$_2$ (JCPDS no. 49-1642). When the Yb^{3+} content is added to 2 and 4 mol%, the phase of the phosphor is also a mixture of monoclinic and cubic phase. However, the proportion of the ingredients is different. The fraction of monoclinic phase in the sample should be given by Garvie *et al*:[12]

$$C_{\mathrm{m}} = \frac{I_{\mathrm{m}}(-111) + I_{\mathrm{m}}(111)}{I_{\mathrm{m}}(-111) + I_{\mathrm{m}}(111) + I_{\mathrm{c}}(111)}.$$

And the fraction of cubic phase is calculated by:

$$C_{\mathrm{c}} = 1 - C_{\mathrm{m}},$$

where m and c stand for monoclinic and cubic phase of the host and *I* stands for the integrated intensity of each peak. The calculated results are shown in table 1. From table 1, we can see that the content of cubic phase of the samples become more with the Yb^{3+} doping concentration increasing. And continued to increase the amount of Yb^{3+} under the same conditions, the phase of the ZrO$_2$:Yb^{3+}-Ho^{3+} samples converted to the pure cubic phase. This confirms the influence of Yb^{3+} ion doping concentration on regulating phase.

SEM showed that the morphology of the sample was elliptical spherical about 50 nm in size and the powder particles are aggregate (see figure 2a). EDS reveal that the chemical composition of the sample contained Zr, O, Yb and Ho (see figure 2b). The results indicated that Yb^{3+} and Ho^{3+} have been effectively incorporated into the ZrO$_2$ host lattice, agreeing with the XRD analysis above.

3.2 *Raman spectra*

In order to investigate the phonon frequency of as-obtained ZrO$_2$ samples, Raman spectra were measured. Figure 3 shows the Raman spectra of the ZrO$_2$:Yb^{3+}-Ho^{3+} (the mole ratio Yb:Ho = 1:1 and 12:1) nanocrystals. For cubic ZrO$_2$:12mol%Yb^{3+}-1mol%Ho^{3+}, their Raman bands are lying at 141, 248, 316, 460 and 628 cm^{-1}. These peaks are similar to Ce$_{1-x}$Zr$_x$O$_2$ ($x = 0.4$–0.7) with fluorite cubic phase.[13] The result indicated that the maximum phonon frequency of cubic ZrO$_2$ is about 628 cm^{-1}. For ZrO$_2$:1mol%Yb^{3+}-1mol%Ho^{3+} of mixed (monoclinic and cubic) phase, the maximum phonon frequency of monoclinic ZrO$_2$ is about 742 cm^{-1}, which is similar to pure ZrO$_2$ with monoclinic phase.[14] The maximum phonon frequency of tetragonal ZrO$_2$ is about 643 cm^{-1}.[15] Compared with the
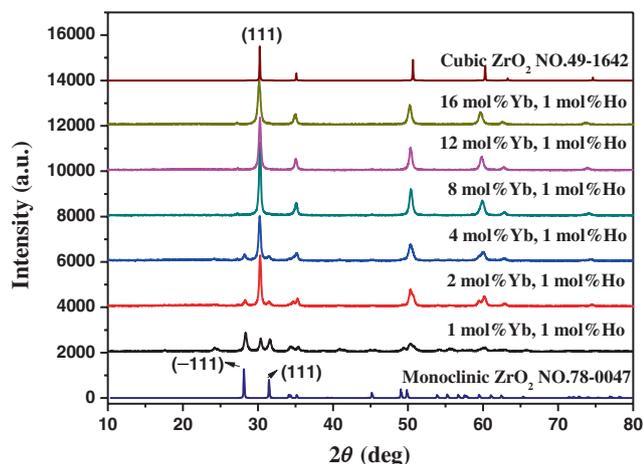
Table 1. The calculated results of content of cubic and monoclinic in ZrO$_2$:Yb^{3+}-Ho^{3+}.

| Sample | Cubic $I_{\mathrm{c}}(111)$ | Monoclinic | | Content of cubic (%) | Content of monoclinic (%) |
		$I_{\mathrm{m}}(-111)$	$I_{\mathrm{m}}(111)$		
ZrO$_2$: Yb^{3+}-Ho^{3+}(1:1)	57	100	69	25.2	74.8
ZrO$_2$: Yb^{3+}-Ho^{3+}(2:1)	100	14	11	80.0	20.0
ZrO$_2$: Yb^{3+}-Ho^{3+}(4:1)	100	15	9	80.6	19.4
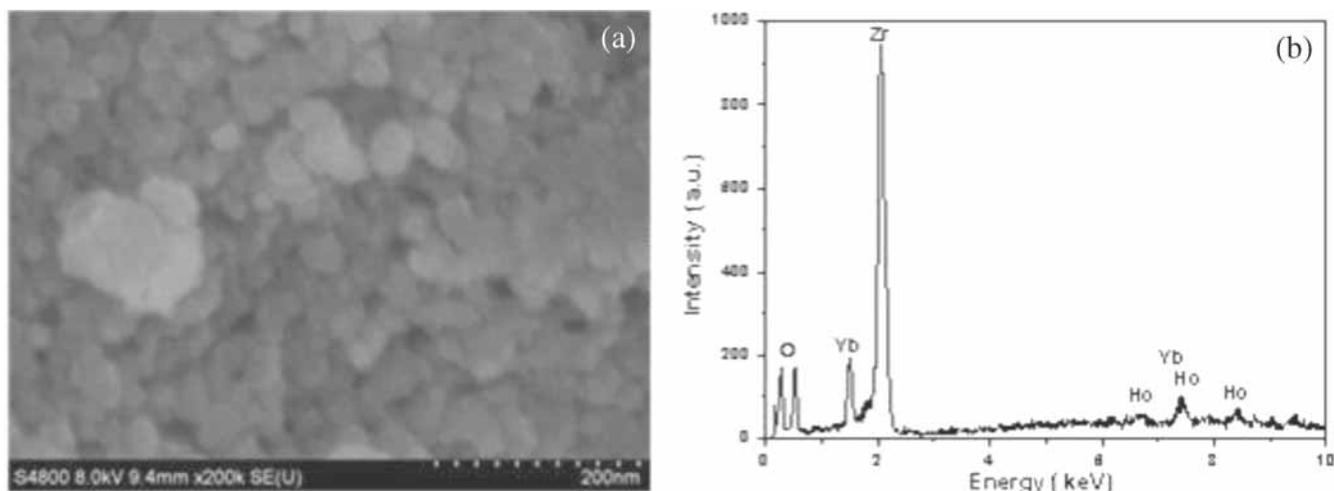
Figure 2. (**a**) SEM image and (**b**) EDS pattern of ZrO_2:Yb^{3+}-Ho^{3+} nanocrystals.
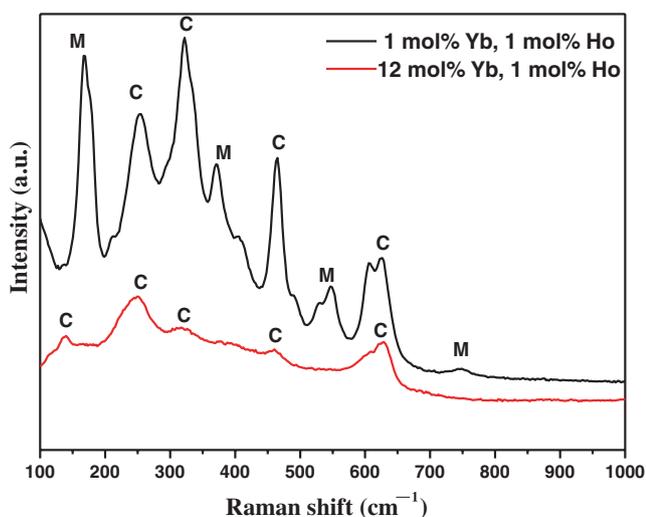
Figure 3. Raman spectra of ZrO_2:1mol%Yb^{3+}-1mol%Ho^{3+} with mixed phase of monoclinic (M) and cubic (C) and ZrO_2:12mol%Yb^{3+}-1mol%Ho^{3+} with representative cubic phase.

Figure 4. Emission spectra of ZrO_2:Yb^{3+}-Ho^{3+} phosphors for different Yb^{3+} doping.

maximum phonon frequency of other oxides ($CaMoO_4$ 815 cm^{-1}; YPO_4 1091 cm^{-1}),[16,17] the maximum phonon frequency of cubic ZrO_2 host (628 cm^{-1}) is relatively low. Generally, the low phonon frequency of host lattice may lead to strong UC emission. Therefore, cubic ZrO_2 is selected as UC host materials.

3.3 *UC luminescence properties*

Figure 4 shows the UC emission spectra of the ZrO_2:Yb^{3+}-Ho^{3+} nanocrystals with the different Yb^{3+} doping concentration and the fixed 1 mol% of Ho^{3+} after excitation at 980 nm. For all the phosphors, there were three emission bands centred at about 539.0, 670.5 and 759.5 nm, which were assigned to $^5S_2$/$^5F_4$ to $^5I_8$, $^5F_5$ to $^5I_8$ and ($^5S_2$/$^5F_4$) to $^5I_7$ transitions, respectively. Among them, the peak located

at 539 nm is the most intense one. What is more, we can see from figure 4 and the inset that, the peaks of the emission spectra of samples roughly keep the similar shape, but the intensity is different. The intensity of emission spectra is increased with the Yb^{3+} doping concentration increasing until 12 mol%. When the Yb^{3+} doping concentration is higher above 12 at.%, the luminescence intensity reduces contrarily owing to the concentration quenching.[18] So we concluded the optimum doping concentration of Yb^{3+} to be about 12 mol%.
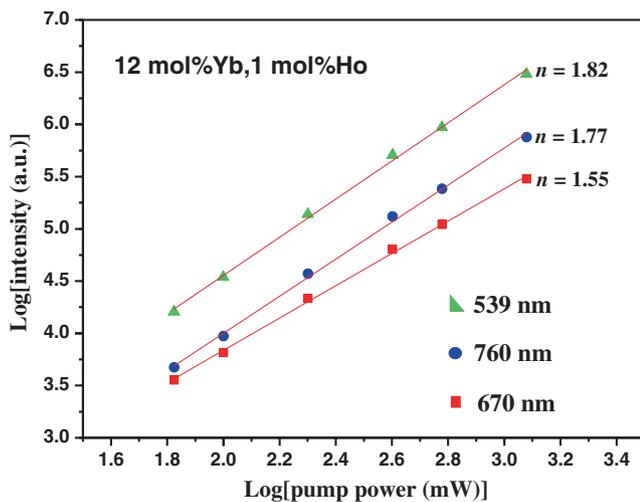
To explore the relation between the UC luminescence and crystal phase, we analyse the emission spectra of ZrO_2:(1, 2, 12 mol%) of Yb^{3+}-1 mol% Ho^{3+}, which stand for typically mixture and pure cubic phase, respectively (figure 5). From figure 5, it can be seen that the emission peaks at 558 and 561 nm are disappeared when the phase of ZrO_2:Yb^{3+}-Ho^{3+} converted from mixture phase to pure cubic. Here, we can definitely say, Yb^{3+} doping concentration has played an important role in the generation of new UC emission band. A similar phenomenon was observed in Yb^{3+} and Tm^{3+} co-doped ZrO_2.[9]

3.4 *UC luminescence mechanism*

It is known that the UC intensity (I) depends on the excitation power (P) according to the power law: $I \approx P^n$,[19] where the number of pumping photons (n) required to excite ions from the ground state to the emitting state can be determined from the slope of the photoluminescence intensity *vs.* the laser excitation power in a log–log plot. The change points of the fluorescence intensity of each band for ZrO$_2$:(12 mol%)Yb^{3+}-(1 mol%)Ho^{3+} *vs.* the logarithm of pump power (log[pump power]) and the fitting results are shown in figure 6. From figure 6, it can be seen that the n values corresponding to the behaviours of the green, red and NIR emission are 1.82, 1.77 and 1.55, respectively, which indicate the presence of a two-photon absorption mechanism in the UC emission.

The generation of the emission channels from the ZrO$_2$:Yb^{3+}-Ho^{3+} system is well explained with the help of the energy level diagrams shown in figure 7. At first, Ho^{3+} is excited from the ground state ($^5I_8$ level) to the excited state ($^5I_6$ level) via the energy transfer from the excited level $^2F_{5/2}$ of Yb^{3+}. The process can be simply expressed as:

$$^2F_{7/2}(Yb^{3+}) + h\upsilon \rightarrow {}^2F_{5/2}(Yb^{3+}). \quad (1)$$

$$^2F_{5/2}(Yb^{3+}) + {}^5I_8(Ho^{3+}) \rightarrow {}^2F_{7/2}(Yb^{3+}) + {}^5I_6(Ho^{3+}). \quad (2)$$

As soon as the $^5I_6$ level gets populated, two different ways of electronic depopulation occur. The first way is that part of
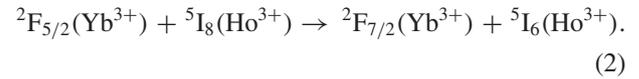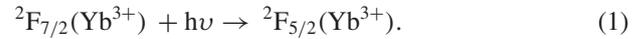

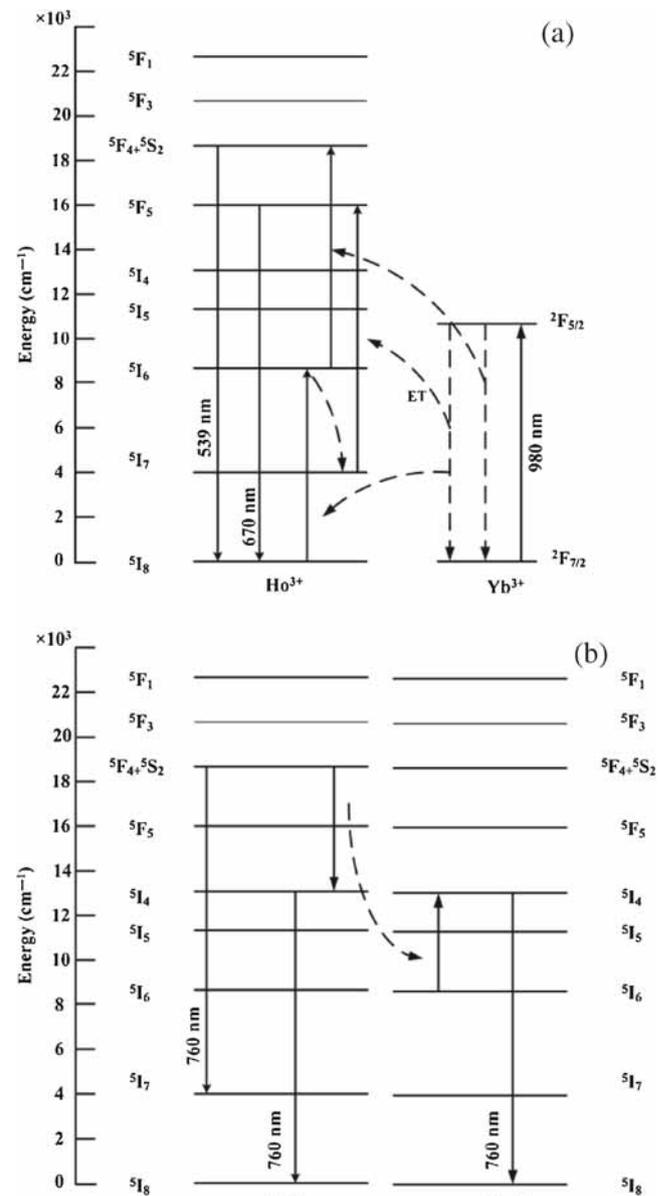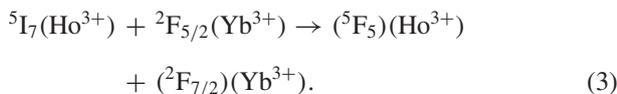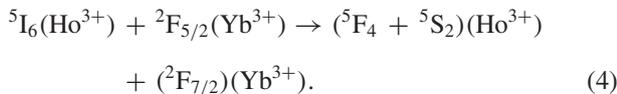**Figure 5.** Emission spectra of typical phase pumped by the same power (1.2 W).

Figure 6. Dependence of the upconverted fluorescence intensity on excitation power under 980 nm excitation for ZrO$_2$:(12 mol%)Yb^{3+}-(1 mol%)Ho^{3+}.

Figure 7. Energy level diagrams for the proposed UPC mechanism: (**a**) energy transfer diagram of Yb^{3+} to Ho^{3+} and (**b**) cross-relation process among Ho^{3+} and Ho^{3+} ions.

Ho^{3+} relaxes to the ^{5}I$_7$ level via non-radiative mechanism. The ^{5}I$_7$ excited ions usually can accept the energy transfer from Yb^{3+} located at excited state and transit to ^{5}F$_5$ level and from there relaxes to the ground state, producing red emission band centred at 671 nm. The mechanism can described as:
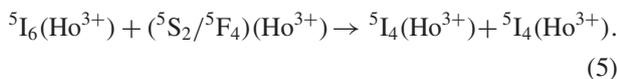
$$^5\text{I}_7(\text{Ho}^{3+}) + {}^2\text{F}_{5/2}(\text{Yb}^{3+}) \rightarrow ({}^5\text{F}_5)(\text{Ho}^{3+})$$
$$+ ({}^2\text{F}_{7/2})(\text{Yb}^{3+}). \tag{3}$$

The second way is that part of the ^{5}I$_6$ excited ions accept directly energy transfer from Yb^{3+} located at excited state and transit to ^{5}S$_2$/^{5}F$_4$ level, it means:

$$^5\text{I}_6(\text{Ho}^{3+}) + {}^2\text{F}_{5/2}(\text{Yb}^{3+}) \rightarrow ({}^5\text{F}_4 + {}^5\text{S}_2)(\text{Ho}^{3+})$$
$$+ ({}^2\text{F}_{7/2})(\text{Yb}^{3+}). \tag{4}$$

The Ho^{3+} located at ^{5}S$_2$/^{5}F$_4$ level transit to the ^{5}I$_8$ level, producing green emission band centred at 540 nm.

In general, ^{5}I$_6$ level lifetime is 5 ms order of magnitude.[20] Ho^{3+} located at this level has a greater likelihood to continue absorbing energy, i.e., more conductive to realize ^{5}S$_2$/^{5}F$_4$ level. So we observed in the emission spectra that the emission intensity of green emission is more intense than that of red emission.

From the aspects of energy matching, Ho^{3+} ions have two transition ways to emit NIR light, shown in figure 7b. One way is that Ho^{3+} located at ^{5}S$_2$/^{5}F$_4$ level transit to ^{5}I$_7$ metastable level, and at the same time Ho^{3+} emitted NIR emission centred at 761 nm. The second way is ^{5}I$_4$ $\rightarrow$ ^{5}I$_8$, namely, ^{5}I$_6$ level and ^{5}S$_2$/^{5}F$_4$ level undergo cross-relaxation to realize ^{5}I$_4$ level. The process is explained as:

$$^5\text{I}_6(\text{Ho}^{3+}) + ({}^5\text{S}_2/{}^5\text{F}_4)(\text{Ho}^{3+}) \rightarrow {}^5\text{I}_4(\text{Ho}^{3+}) + {}^5\text{I}_4(\text{Ho}^{3+}). \tag{5}$$

The Ho^{3+} located at ^{5}I$_4$ level transit to the ground state (^{5}I$_8$ level) producing NIR light about 761 nm.

4. Conclusion

In summary, the ZrO$_2$:Yb^{3+}-Ho^{3+} phosphors with different Yb^{3+} doping concentrations have been synthesized by co-precipitation method. XRD patterns were shown that when the concentration of Yb^{3+} were 1, 2 and 4 mol% in the case of the fixed 1 mol% of Ho^{3+}, the samples were a mixture of monocline and cubic phase. Continued to increase Yb^{3+} concentration, the host was stable to cubic phase. We have also confirmed that the emission peaks at 558 and 561 nm were disappeared when the phase of ZrO$_2$:Yb^{3+}-Ho^{3+} converted from mixture phase to pure cubic. The values of pumping photons (n) indicated that two excitation photons are involved in the UC process. In conclusion, concentration of Yb^{3+} ions has played a major role in the regulation phase and upconverted emission in Yb^{3+}-Ho^{3+} co-doped ZrO$_2$ nanocrystals.

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