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Upconversion Luminescence Properties of Ho^{3+}, Tm^{3+}, Yb^{3+} Co-Doped Nanocrystal $NaYF_4$ Synthesized by Hydrothermal Method

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Abstract: Nanocrystal of upconversion (UC) phosphor Ho^{3+}, Tm^{3+}, and Yb^{3+} co-doped $NaYF_4$ was prepared by the hydrothermal method in the presence of the complexing agent EDTA. Under 980 nm diode laser excitation, the impact of different concentrations of Ho^{3+} ion on the UC luminescence intensity was discussed. The log of luminescence intensity versus pump power show that the 474 nm blue emission, 538 nm green emission, and 652 nm red emission are all due to the two-photon process, while the 450 nm blue emission is a three-photon process. The UC mechanism and processes were also analyzed. The sample was characterized by transmission electron microscopy (TEM) and X-ray diffraction (XRD). The result shows that Ho^{3+}, Tm^{3+}, and Yb^{3+} co-doped $NaYF_4$ prepared by the hydrothermal method exhibits a hexagonal nanocrystal.

Key words: hydrothermal method; upconversion; EDTA; Nanocrystal; $NaYF_4$:Ho^{3+}, Tm^{3+}, Yb^{3+}; rare earths
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In recent years, great attention has been paid to upconversion (UC) luminescence materials for their applications in solid-state laser, display, communications, and so on[1]. The recent researches centering at the intersection of nanotechnology and biotechnology are opening up a new period for the development of UC[2,3]. When compared with the traditional materials, the nano materials have better properties in terms of optics, electricity, structure, and so on due to their physical and chemical features. So, the near-infrared to visible UC nanomaterials have significant applications to the area of infrared detection and biological label[4,5].

Rare earth-doped materials have gained further interest for their frequency conversion through UC mechanisms. These mechanisms involve a sensitization of photons usually taking place by the transfer of energy in rare earth ion pairs. A study on the energy transfer processes enables for a further understanding of the UC mechanisms in general and leads to better tailored UC materials. As known, the controlled fabrication of a host with almost structure is important for enhancing the upconversion efficiency, because the phonon in the material will give rise to nonradiative decay to suppress UC luminescence. Therefore, it is necessary to choose a lattice with much lower phonon energy in order to overcome the decay problem. Since early 1970s, the hexagonal $NaYF_4$ has been discovered, showing a high refractive index and low phonon energy, and has been regarded as an excellent host matrix for performing infrared to visible upconversion as activated by Yb^{3+}/

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Er^{3+} ion pairs[6-11], Yb^{3+}, Tm^{3+} co-doped hexagonal phase $NaYF_4$ nanoparticles have recently been synthesized by the precipitation method[12].

In the present study, Ho^{3+}, Tm^{3+}, Yb^{3+} co-doped $NaYF_4$ nanocrystal UC phosphor was prepared via the hydrothermal method. The hydrothermal synthesis method is a new method for the preparation of UC host materials because its process can be carried out at low temperatures and the process of operation is also easy[13]. In addition, it can prevent host materials from oxidization[14]. Transmission electron microscopy (TEM) and X-ray diffraction (XRD) were used to characterize the nanoparticles. The UC spectrum was recorded on a Hitachi F-4500 spectrophotometer. The UC mechanisms of Ho^{3+}, Tm^{3+}, Yb^{3+} co-doped $NaYF_4$ nanoparticles were also discussed.

1 Experimental

NaF, NH_4HF_2, and EDTA of AR grade were obtained from Beijing Chemical Plant. Y_2O_3, Yb_2O_3, Ho_2O_3, and Tm_2O_3(99.9%) were obtained from General Research Institute of Nonferrous Metals. Ho^{3+}, Tm^{3+}, Yb^{3+} co-doped $NaYF_4$ nanoparticles were prepared by hydrothermal synthesis using EDTA as the complexing agent. The mixture ratio of the reactants was as follows: $(1-x-y-z)Y_2O_3 + 3NH_4HF_2 + 2NaF_2 + xHo_2O_3 + yYb_2O_3 + zTm_2O_3 + 2EDTA$. y and z was equal to 0.02 and and 0.04 mol, respectively, while x varies from 0.002 mol to 0.006 mol. First, mixing and stirring the reactants were managed. Then, the pH value was adjusted to 4 with hydrofluoric acid. Finally, the mixture was sealed in Teflon-lined stainless steel autoclaves and heated at 220 ℃ for a d. The product was filtered, washed, and dried and the final product was then obtained.

The XRD pattern was obtained on D/max 2500VPC X-ray Diffractometer, using Cu Kα radiation from a rotating anode. Investigations on the particle size and morphology were performed using a JEM-2010 transmission electron microscope. The UC spectrum was taken on a Hitachi F-4500 spectrophotometer.

2 Results and Discussion

The XRD pattern (Fig. 1) shows that hexagonal $NaYF_4$ was prepared using hydrothermal synthesis. It is basically consistent with the JCPDS standard card No. 27-0689. The XRD pattern of $NaYF_4$ had little change following co-doping with Ho^{3+}, Tm^{3+}, and Yb^{3+} ions. From the XRD pattern, it can be concluded that the sample is well crystallized. All the peaks could be readily indexed to the hexagonal $NaYF_4$ phase . The

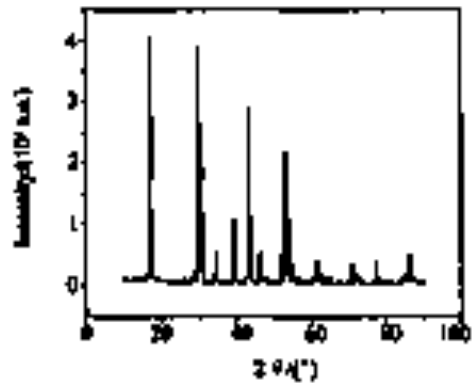

Fig.1 XRD pattern of Ho^{3+}, Tm^{3+}, Yb^{3+} co-doped $NaYF_4$ sample

grain size was calculated using the Debye-Scherrer equation: $D = \frac{K\lambda}{\beta\cos\theta}$. The grain size was about 30 nm.

Fig.2(a) shows the TEM photo of Ho^{3+}, Tm^{3+}, Yb^{3+} co-doped $NaYF_4$ without EDTA, where a lot of agglomerated particles were visible. The agglomerated nanoparticle size was about 300 ~ 500 nm. In this study, the nanocrystal of upconversion phosphor Er^{3+}, Tm^{3+}, and Yb^{3+} co-doped $NaYF_4$ was prepared by the hydrothermal method in the presence of complexing agent EDTA. EDTA is a strong complexing agent to the rare earth ions. When the molar ratio of EDTA/Ln^{3+} was 1, small nanoparticles were generated. The size of the nanoparticle is about 50 nm, as shown in Fig.2(b). Fig.2(c) shows the room crystal diffraction pattern of Ho^{3+}, Tm^{3+}, Yb^{3+} co-doped $NaYF_4$ sample. The symmetrical characteristics of the diffraction spots were analyzed, and it can be confirmed that hexagonal $NaYF_4$ was prepared using hydrothermal synthesis.

Fig.3 shows the UC emission spectrum recorded under the excitation by 980 nm diode beam. Four peaks at 450, 474, 538, and 642 nm were observed on the profile. Among the emission peaks in the visible range, the peak around 538 nm was the most intense.

Fig.4 shows the UC spectrums of Ho^{3+}, Tm^{3+}, Yb^{3+} co-doped $NaYF_4$ with different concentrations of Ho^{3+} ion excited by 980 nm. When the molar ratio is 0.6% Ho^{3+}, 2% Yb^{3+}, 4% Tm^{3+}, the intensity of green emission is the most intense. While the molar ratio is 0.5% Ho^{3+}, 2% Yb^{3+} and 4% Tm^{3+}, the intensity of blue emission is the most intense. When compared with the green and blue emission, the red emission is rather weak.

The UC intensity depends on the pumping power (Fig.5). The relationship between them can be ex-

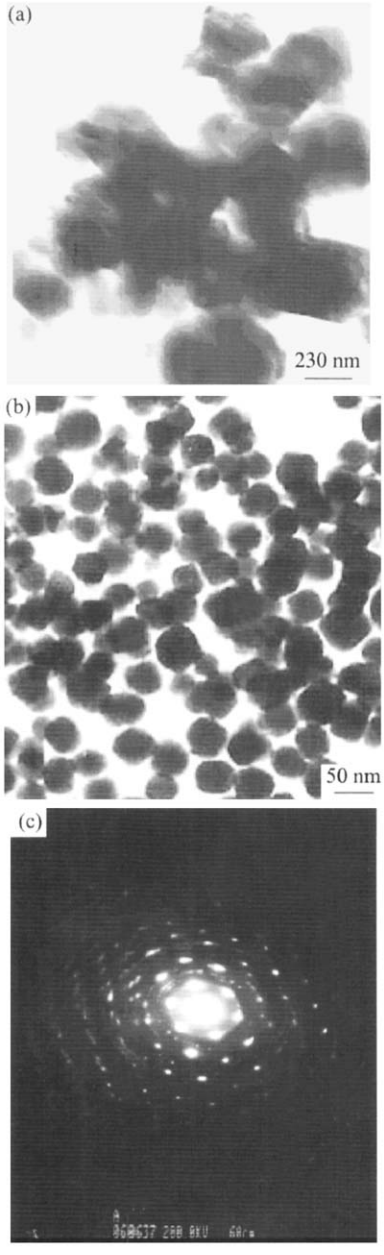

Fig.2 TEM photo of Ho^{3+}, Tm^{3+}, Yb^{3+} co-doped $NaYF_4$ sample

(a) TEM photo of Ho^{3+}, Tm^{3+}, Yb^{3+} co-doped $NaYF_4$ sample without EDTA; (b) TEM photo of Ho^{3+}, Tm^{3+}, Yb^{3+} co-doped $NaYF_4$ sample with EDTA; (c) Unit crystal diffraction pattern of Ho^{3+}, Tm^{3+}, Yb^{3+} co-doped $NaYF_4$ sample

proximately expressed as follows: $I_{up} \propto (I_{ir})^n$, where n is the number of infrared photons absorbed for emitting a visible photon, I_{up} the output intensity and I_{ir} the infrared excitation intensity. In the double-log coordinate, the slope of I_{up}-I_{ir} indicates the value of n. Through the value of n, it can be concluded that the 474 nm blue emission, 538 nm green emission, and 642 nm red emission are all two-photon processes, while the 450 nm blue emission is a three-photon process.

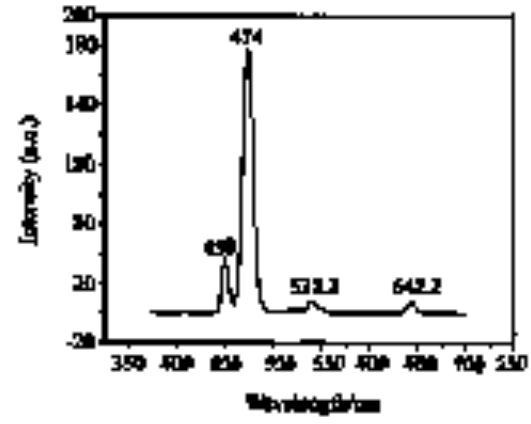

Fig.3 Upconversion spectrum of Ho^{3+}, Tm^{3+}, Yb^{3+} co-doped $NaYF_4$ excited by 980 nm

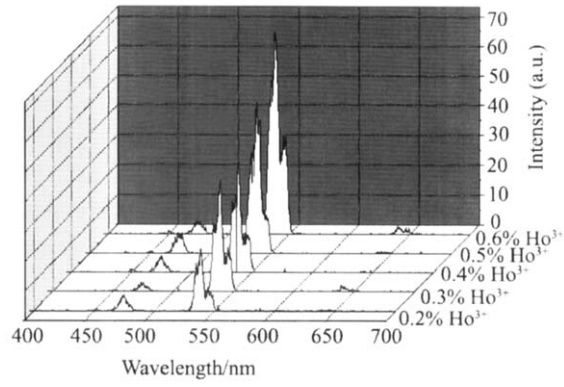

Fig.4 Upconversion emission spectrum of Ho^{3+}, Tm^{3+}, Yb^{3+} co-doped $NaYF_4$ with different concentrations of Ho^{3+} ion excited by 980 nm

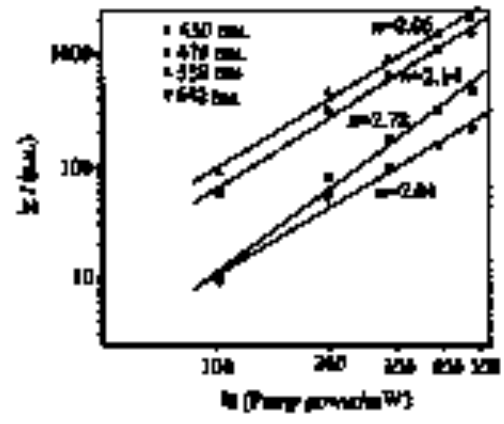

Fig.5 Log-log plot of upconversion emission intensity as a function of excitation power at 980 nm for Ho^{3+}, Tm^{3+}, Yb^{3+} co-doped $NaYF_4$ sample

The possible upconversion mechanisms of the Ho^{3+}, Tm^{3+}, Yb^{3+} co-doped $NaYF_4$ nanoparticles are shown in Fig.6. Under the 980 nm excitation, electrons of Yb^{3+} ions excited from $^2F_{7/2}$ to $^2F_{5/2}$ level. The excitation energy could be nonradiatively transferred to the corresponding excited level of Tm^{3+} and Ho^{3+} ions. The emission bands at 450, 474, 538, and 642 nm

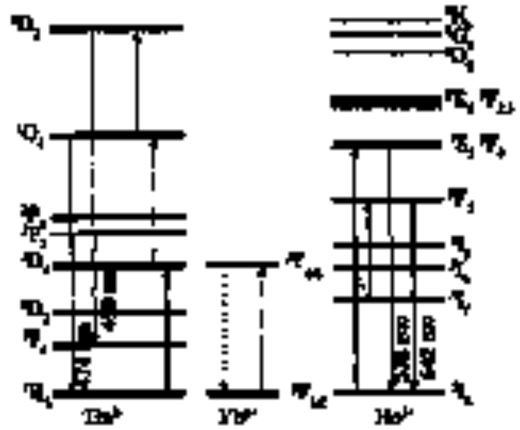

Fig. 6 Upconversion mechanism of Ho^{3+}, Tm^{3+}, Yb^{3+} co-doped $NaYF_4$ at 980 nm excitation

would be assigned to ${}^1D_2 \rightarrow {}^3F_4$, ${}^1G_4 \rightarrow {}^3H_6$, ${}^1G_4 \rightarrow {}^3H_4$, and ${}^5F_5 \rightarrow {}^5I_8$ transitions of Tm^{3+} and Ho^{3+} ion, respectively. This mechanism is in good agreement with the slopes of 2.78 for 450 nm, 2.14 for 474 nm, 2.09 for 538 nm, and 2.04 for 642 nm, which are derived from the experimental data in the double logarithmic plots. The possible UC channels are as follows:

(i) The UC channel of 450 nm blue emission

${}^2F_{7/2}(Yb^{3+}) + 980$ nm photon $\rightarrow {}^2F_{5/2}(Yb^{3+})$

${}^2F_{5/2}(Yb^{3+}) + {}^3H_6(Tm^{3+}) \rightarrow {}^2F_{7/2}(Yb^{3+}) + {}^3H_5(Tm^{3+})$

${}^2F_{5/2}(Yb^{3+}) + {}^3H_4(Tm^{3+}) \rightarrow {}^2F_{7/2}(Yb^{3+}) + {}^1G_4(Tm^{3+})$

${}^2F_{5/2}(Yb^{3+}) + {}^1G_4(Tm^{3+}) \rightarrow {}^2F_{7/2}(Yb^{3+}) + {}^1D_2(Tm^{3+})$

${}^1D_2(Tm^{3+}) \rightarrow {}^3F_4(Tm^{3+}) + 450$ nm photon

(ii) The UC channel of 474 nm blue emission

${}^2F_{7/2}(Yb^{3+}) + 980$ nm photon $\rightarrow {}^2F_{5/2}(Yb^{3+})$

${}^2F_{5/2}(Yb^{3+}) + {}^3H_6(Tm^{3+}) \rightarrow {}^2F_{7/2}(Yb^{3+}) + {}^3H_5(Tm^{3+})$

${}^2F_{5/2}(Yb^{3+}) + {}^3H_4(Tm^{3+}) \rightarrow {}^2F_{7/2}(Yb^{3+}) + {}^1G_4(Tm^{3+})$

${}^1G_4(Tm^{3+}) \rightarrow {}^3H_6(Tm^{3+}) + 474$ nm photon

(iii) The UC channel of 538 nm green emission

${}^2F_{7/2}(Yb^{3+}) + 980$ nm photon $\rightarrow {}^2F_{5/2}(Yb^{3+})$

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

${}^2F_{5/2}(Yb^{3+}) + {}^5I_6(Ho^{3+}) \rightarrow {}^2F_{7/2}(Yb^{3+}) + {}^5F_4(Ho^{3+})$

${}^5F_4(Ho^{3+}) \sim {}^5S_2(Ho^{3+})$

${}^5S_2(Ho^{3+}) \rightarrow {}^5I_8(Ho^{3+}) + 538$ nm photon

(iv) The UC channel of 642 nm red emission

${}^2F_{7/2}(Yb^{3+}) + 980$ nm photon $\rightarrow {}^2F_{5/2}(Yb^{3+})$

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

${}^5I_6(Ho^{3+}) \sim {}^5I_7(Ho^{3+})$

${}^2F_{5/2}(Yb^{3+}) + {}^5I_7(Ho^{3+}) \rightarrow {}^2F_{7/2}(Yb^{3+}) + {}^5F_5(Ho^{3+})$

${}^5F_5(Ho^{3+}) \rightarrow {}^5I_8(Ho^{3+}) + 642$ nm photon

3 Conclusion

In the present study, the successful synthesis of Ho^{3+}, Tm^{3+}, Yb^{3+} ions co-doped $NaYF_4$ nanocrystal prepared by hydrothermal method in the presence of complexing agent EDTA was reported. The sample was characterized by TEM and XRD. The result shows that hexagonal nanocrystal Ho^{3+}, Tm^{3+}, Yb^{3+} co-doped $NaYF_4$ was prepared with the particle size of about 50 nm. The UC luminescence intensity increases as the Ho^{3+} concentration increases and reaches its peak at 0.5% (mole fraction). According to the law of luminescence intensity versus pump power, 474 nm blue emission, 538 nm green emission, and 642 nm red emission are all two-photon processes, while the 450 nm blue emission is a three-photon process.

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