



# Tunable red-green-blue multicolor luminescence in $\text{Yb}^{3+}/\text{Tm}^{3+}/\text{Ho}^{3+}:\text{Gd}_3\text{Ga}_5\text{O}_{12}$ nano-crystals

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## ARTICLE INFO

### Article history:

Received 26 May 2011

Received in revised form

15 September 2011

Accepted 19 September 2011

Available online 22 September 2011

### Keywords:

$\text{Tm}^{3+}/\text{Ho}^{3+}/\text{Yb}^{3+}:\text{Gd}_3\text{Ga}_5\text{O}_{12}$

Multicolor up-conversion

Energy transfer

## ABSTRACT

The  $\text{Yb}^{3+}/\text{Tm}^{3+}/\text{Ho}^{3+}:\text{Gd}_3\text{Ga}_5\text{O}_{12}$  nano-crystals have been successfully prepared via a citric acid complex procedure. The luminescence spectra were measured and the up-conversion processes were discussed. By means of adjusting the doping concentrations of  $\text{Yb}^{3+}/\text{Tm}^{3+}/\text{Ho}^{3+}$ , the red-green-blue up-conversion luminescence changed obviously. Results indicated that the ratio of red-green-blue up-conversion emissions enhanced heavily with the increasing concentrations of  $\text{Tm}^{3+}$  doped in the  $\text{Yb}^{3+}/\text{Tm}^{3+}/\text{Ho}^{3+}:\text{Gd}_3\text{Ga}_5\text{O}_{12}$  nano-crystals, which was rooted in the three-photon resonant cross relaxation processes ( $^1\text{G}_4(\text{Tm}) + ^5\text{I}_7(\text{Ho}) \rightarrow ^3\text{H}_5(\text{Tm}) + ^5\text{S}_2(\text{Ho})$ ). The tunable red-green-blue luminescence could be used in the fields of display, illumination, and photonics such as the white light generation.

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## 1. Introduction

During the last decade there has been an extensive interest in the investigation of lanthanide-based phosphors to be used for a wide range of potential applications, such as multicolor displays, fluorescence imaging for detection of biomolecules, optical data storage, back lighting, and so on [1–5]. Three fundamental red, green, and blue light colors in these phosphors could be conveniently available by doping with  $\text{Eu}^{3+}$ ,  $\text{Tm}^{3+}$ ,  $\text{Er}^{3+}$ ,  $\text{Ce}^{3+}$ ,  $\text{Pr}^{3+}$  ions and so on [6–9]. However, the simultaneous generation of red-green-blue emission via single wavelength excitation was scarcely demonstrated since different energy-transfer and cross-relaxation processes were exhibited when these rare earth ions were implanted into different host materials. Recently, white up-conversion luminescence have been demonstrated in  $\text{Yb}^{3+}$ ,  $\text{Ho}^{3+}$  and  $\text{Tm}^{3+}$  ions doped fluoride, germanate and tellurite glass [10,11]. Particularly, a weak blue luminescence has been observed in the tellurite glass under excitation of 980 nm, which suggest that there is some potential multicolor application.

In our study,  $\text{Gd}_3\text{Ga}_5\text{O}_{12}$  phosphor was chosen as the host material to investigate the multicolor luminescence.  $\text{Gd}_3\text{Ga}_5\text{O}_{12}$  is well known as an important class of materials for advanced optical technologies [12]. There are large available literatures on the up-conversion luminescence characterization of  $\text{Re}^{3+}$ -doped

$\text{Gd}_3\text{Ga}_5\text{O}_{12}$ . Here we reported for the first on the design of blue, green and red up-conversion luminescence in  $\text{Gd}_3\text{Ga}_5\text{O}_{12}$  powder doped with  $\text{Yb}^{3+}/\text{Ho}^{3+}/\text{Tm}^{3+}$  ions under NIR (971.5 nm) excitation and presented the multicolor up-conversion luminescence mechanisms.

## 2. Experimental

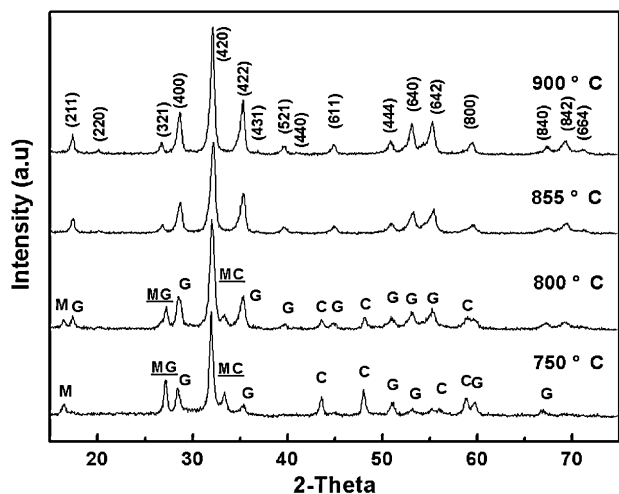
### 2.1. Chemicals

The starting materials were Gadolinium oxide ( $\text{Gd}_2\text{O}_3$ , 99.999%), holmium oxide ( $\text{Ho}_2\text{O}_3$ , 99.99%), thulium oxide ( $\text{Tm}_2\text{O}_3$ , 99.9%), ytterbium oxide ( $\text{Yb}_2\text{O}_3$ , 99.99%), gallium nitrate ( $\text{Ga}(\text{NO}_3)_3 \cdot \text{H}_2\text{O}$ , 99.99%), hydrated citric acid ( $\text{C}_6\text{H}_8\text{O}_7 \cdot \text{H}_2\text{O}$ , AR grade) and ammonia ( $\text{NH}_4\text{NO}_3$ , AR grade). Citric acid was used as complex agent for the xerogel process and fuel for combustion.

### 2.2. Sample preparation

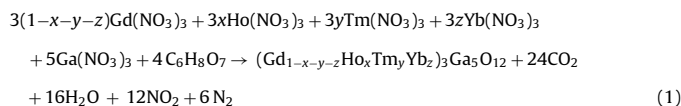
$\text{Gd}_3\text{Ga}_5\text{O}_{12}$  powder samples doped with (1) 5 at.%  $\text{Yb}^{3+}$  and  $x$  at.%  $\text{Ho}^{3+}$  ( $x = 0.05, 0.5$  and  $2.5$ ); (2) 5 at.%  $\text{Yb}^{3+}$  and 1.0 at.%  $\text{Tm}^{3+}$ ; (3) 5 at.%  $\text{Yb}^{3+}$ , 0.05 at.%  $\text{Ho}^{3+}$  and  $y$  at.%  $\text{Tm}^{3+}$  ( $y = 0.5, 1.0, 1.5, 2.0$  and  $2.5$ ) ions were prepared by using a citric acid complex procedure described briefly as follows. Firstly,  $\text{Gd}_2\text{O}_3$ ,  $\text{Ho}_2\text{O}_3$ ,  $\text{Yb}_2\text{O}_3$  and  $\text{Tm}_2\text{O}_3$  were dissolved in nitric acid to obtain the corresponding rare earth nitrate solution, respectively. Gadolinium, gallium, holmium, thulium and ytterbium nitrates with stoichiometric mole ratio of cations were completely mixed to form mixed solution. Certain amount of citric acid, the molar ratio of which to total metal cation was 1:1, was added into the mixed nitrate solution. The pH of the solution was further adjusted to 3 by ammonium hydroxide. The solution was continuously stirred at 90 °C for several hours until it turned to sticky yellow sol. Then, the sol was dried at 100 °C for 24 h to obtain the brown xerogel. The xerogel was ground into powders, put into a furnace for pre-calcination at 250 °C for about 30 min, and then calcined at the required temperatures from 750 to 900 °C. As the ignition occurred, the reaction went on vigorously for a few seconds. Then, the white and very fluffy products

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**Fig. 1.** XRD patterns of  $Gd_3Ga_5O_{12}$  phosphor samples calcinated at different temperatures.

were obtained after the combustion reaction. The products were lightly ground to powder in a mortar for tests. Finally, the rare-earth-doped  $Gd_3Ga_5O_{12}$  phosphor samples were synthesized. The proposed stoichiometric equation for the synthesis reaction is given below:



where in this case  $x=0.05, 0.5$  and  $2.5$  at.%;  $y=0.5, 1.0, 1.5, 2.0$  and  $2.5$  at.%;  $z=5$  at.%. All samples were kept in air without any further precaution.

### 2.3. Measurements

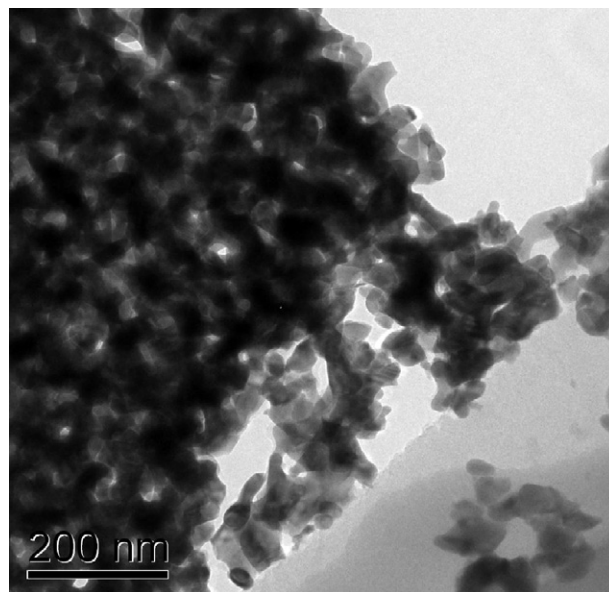
X-ray powder diffraction (XRD) analysis was performed to identify the crystallization phase with a power diffractometer (RIGAKU, DMAX2500PC) operated at 40 kV and 100 mA, using  $Cu\ K\alpha$  as the radiation ( $\lambda = 1.5405 \text{ \AA}$ ). The  $2\theta$  scan range was  $5\text{--}85^\circ$  with a step size of  $0.05^\circ$ . The microstructures of the sample were analyzed by a transmission electron microscope (TEM, JEM-2010). The visible up-conversion fluorescence signals were detected with photomultiplier tubes (PMT, R928) excited by a power-controllable 971.5 nm LD (laser diode) (DPL-II, Module-HTL98M10) with the maximum power of 9 W. All the measurements were carried out at room temperature.

## 3. Results and discussion

The XRD patterns of samples calcinated at various temperatures are shown in Fig. 1. There were a small amount of intermediate-phase cubic  $Gd_2O_3$  (JCPDS Card No.88-2165) and monoclinic  $Gd_4Ga_2O_9$  (JCPDS Card No. 38-0505) in the XRD curves when the calcinated temperature was below  $855^\circ\text{C}$ . When the temperature to exceed  $855^\circ\text{C}$ , all peaks are in good accordance with the standard JCPDS Card (No. 13-0493) of  $Gd_3Ga_5O_{12}$ . The single-phase of cubic  $Gd_3Ga_5O_{12}$  is obtained. Therefore, a calcinated temperature above  $855^\circ\text{C}$  for 10 min was necessary in the present experiments. This indicated that the calcinated temperature has significant effect on the process of crystallization [13]. Additionally, the diffraction peaks become sharper and more intense with an increase of calcinated temperature.

Fig. 2 shows a TEM image of the  $Gd_3Ga_5O_{12}$  nano-crystals doped with 5 at.%  $Yb^{3+}$  and 1 at.%  $Tm^{3+}$  ions heated at  $900^\circ\text{C}$  for 0.5 h. The size of the nano-crystals is found to be approximately 50 nm and tends to aggregate. The size is larger than that estimated from the Scherrer equation (20 nm). The abnormal crystalline encompassed with several pores may give an explanation to the lower values calculated by XRD FWHM analysis [14].

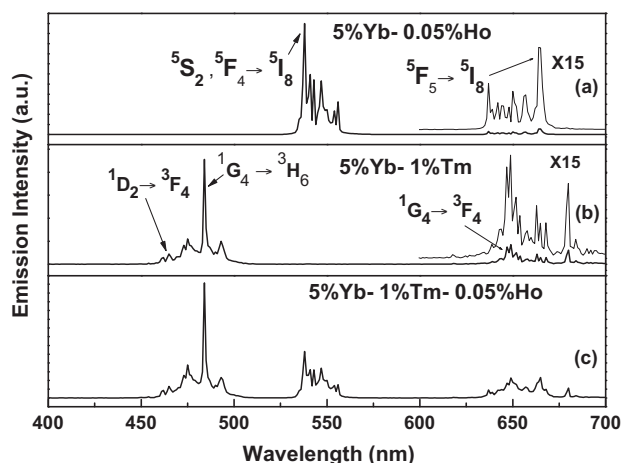
In the complex tri-doped system, the 971.5 nm laser diode was selected as the excitation pump source because of the larger



**Fig. 2.** TEM image of  $Gd_3Ga_5O_{12}$  nano-crystals doped with 5 at.%  $Yb^{3+}$  and 1 at.%  $Tm^{3+}$  ions calcinated at  $900^\circ\text{C}$  for 30 min.

absorption section of  $Yb^{3+}$  ions here than those of  $Tm^{3+}$  and  $Ho^{3+}$  ions. It is well known that  $Yb^{3+}$  ions can efficiently sensitize  $Ho^{3+}$  and  $Tm^{3+}$  ions, respectively [15–17]. The  $Gd_3Ga_5O_{12}$  phosphors tri-doped with  $Yb^{3+}$ ,  $Tm^{3+}$  and  $Ho^{3+}$  ions were prepared and the up-conversion luminescence excited with 971.5 nm was presented in Fig. 3(a–c). Compared with Fig. 3(a and b), the up-conversion bands centered at 465, 484, 538, 665 (630–675) and 649 (640–690) nm in Fig. 3(c) consisted of the compound up-conversion emissions, which were assigned to the intra-4f electronic transitions of  $Tm^{3+}$  and  $Ho^{3+}$  ions, corresponding to the transitions  $^1D_2 \rightarrow ^3F_4$  ( $Tm^{3+}$ ) (465 nm),  $^1G_4 \rightarrow ^3H_6$  ( $Tm^{3+}$ ) (484 nm) for blue up-conversion emissions and  $^1G_4 \rightarrow ^3F_4$  ( $Tm^{3+}$ ) (649 nm) for red up-conversion emission;  $^5F_4/^5S_2 \rightarrow ^5I_8$  ( $Ho^{3+}$ ) (538 nm) for green and  $^5F_5 \rightarrow ^5I_8$  ( $Ho^{3+}$ ) (665 nm) for red up-conversion emission [15–17]. Obviously, the red up-conversion band of 630–675 nm was the overlap joint of  $Tm^{3+}$  and  $Ho^{3+}$ .

In Fig. 3(a and b), the images of 600–700 nm were zoomed in 15 multiplies, shown upward. Here we found an interesting



**Fig. 3.** Up-converted emission spectra of  $Ga_3Gd_5O_{12}$  nano-crystals doped with: (a) 5 at.%  $Yb^{3+}$  and 0.05 at.%  $Ho^{3+}$ , (b) 5 at.%  $Yb^{3+}$  and 1.0 at.%  $Tm^{3+}$ , (c) 5 at.%  $Yb^{3+}$ , 1 at.%  $Tm^{3+}$  and 0.05 at.%  $Ho^{3+}$  ions under diode laser excitation at 971.5 nm with  $6.87\text{ W/cm}^2$ . (Insets are the amplificatory curves for the corresponding red emission range from 600 to 700 nm with 15 times.)

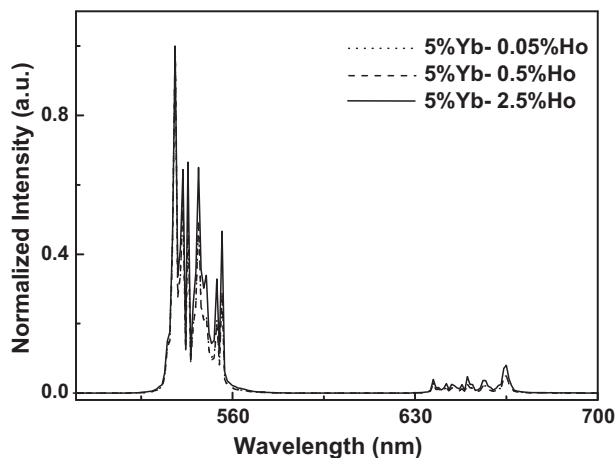


Fig. 4. Normalized up-conversion luminescence of  $\text{Yb}^{3+}:\text{Gd}_3\text{Ga}_5\text{O}_{12}$  ( $\text{Yb}^{3+}$ :5 at.%) doped with 0.05 at.%, 0.5 at.%, and 2.5 at.%  $\text{Ho}^{3+}$  ions excited by 971.5 nm with  $6.87 \text{ W/cm}^2$ .

phenomenon. When co-doped with  $\text{Tm}^{3+}$  and  $\text{Ho}^{3+}$  (Fig. 3(c)), the intensities of red band changed differently, compared with single doped  $\text{Tm}^{3+}$  or  $\text{Ho}^{3+}$  (Fig. 3(a and b)). The intensity of the red emission centered at 650 nm enhanced whereas that of the red emission centered at 680 nm decreased. This was an effective energy transfer process from  $\text{Tm}^{3+}$  to  $\text{Ho}^{3+}$  ions involved in enhancing the red emission of  $\text{Ho}^{3+}$  ions. It may be suggested as a nearly resonant cross relaxation process  $^1\text{G}_4(\text{Tm}) + ^5\text{I}_7(\text{Ho}) \rightarrow ^3\text{F}_4(\text{Tm}) + ^5\text{F}_5(\text{Ho})$ , hereinafter designated as CR1 (see Fig. 8), which is responsible for the red up-conversion emission energy transfer (energy mismatch of  $151 \text{ cm}^{-1}$ ). All facts have been identified by spectral and kinetic investigations, suggesting the occurrence of the proposed cross relaxation process.

As shown in Fig. 3(c), the  $\text{Gd}_3\text{Ga}_5\text{O}_{12}:\text{Yb}^{3+}/\text{Tm}^{3+}/\text{Ho}^{3+}$  nano-crystals could emit red, green, blue luminescence, whereas their intensities were different. In order to tune the relative intensities of red, green, blue, we changed the ratio of the dope ions  $\text{Tm}^{3+}$ ,  $\text{Ho}^{3+}$ . Firstly, we changed the doped concentrations of  $\text{Ho}^{3+}$  ions. Several materials of  $\text{Gd}_{2.85-x}\text{Ho}_x\text{Yb}_{0.15}\text{Ga}_5\text{O}_{12}$  ( $\text{Yb}^{3+}$ :5 at.%), where  $x$  were 0.05 at.%, 0.5 at.%, and 2.5 at.%, were prepared and their normalized up-conversion luminescence excited by 971.5 nm were presented in Fig. 4. The relative intensity ratio of green to red emission in the three samples almost remained constant, which indicated that it was impossible to tune the intensity ratio of the green to red by changing the doped concentration of  $\text{Ho}^{3+}$  ions in the  $\text{Gd}_3\text{Ga}_5\text{O}_{12}:\text{Yb}^{3+}/\text{Tm}^{3+}/\text{Ho}^{3+}$  nano-crystals. And for the same reason, we should change the concentration of  $\text{Tm}^{3+}$  ions. Several materials of  $\text{Gd}_3\text{Ga}_5\text{O}_{12}$  doped with 0.05 at.%  $\text{Ho}^{3+}$  and 0.5 at.%  $\text{Yb}^{3+}$  as well as  $x$  at.%  $\text{Tm}^{3+}$  ions, where  $x$  were 0.5, 1.0, 1.5, 2.0 and 2.5 at.%, were prepared and their normalized up-conversion luminescence excited by 971.5 nm, shown in Fig. 5. The relative intensities of red, green, blue bands changed with the increase of the doped concentration of  $\text{Tm}^{3+}$ . In Fig. 5(b), where the doped concentrations of  $\text{Yb}^{3+}$ ,  $\text{Tm}^{3+}$  and  $\text{Ho}^{3+}$  were 5 at.%, 2.0 at.% and 0.05 at.%, the intensities of red, green, blue were almost equal, which could be used to generate white light.

Fig. 6 shows the calculated 1931 CIE color coordinates of  $\text{Gd}_3\text{Ga}_5\text{O}_{12}$  nanocrystals doped with 5 at.%  $\text{Yb}^{3+}$ , 1 at.%  $\text{Tm}^{3+}$  and 0.05 at.%  $\text{Ho}^{3+}$  ions under diode laser excitation at 971.5 nm with pump powers vary from  $3.33 \text{ W/cm}^2$  to  $30.5 \text{ W/cm}^2$ . The values were calculated to be about (0.26, 0.44) in  $3.33 \text{ W/cm}^2$  and moved toward to (0.20, 0.34) in  $30.5 \text{ W/cm}^2$  (symbols of  $\circ$ ). The colors of the tri-doped  $\text{Gd}_3\text{Ga}_5\text{O}_{12}$  nanocrystals varied from green to bluish green and then turned to blue green with the increasing pump power. Three-photon process was involved to produce the blue

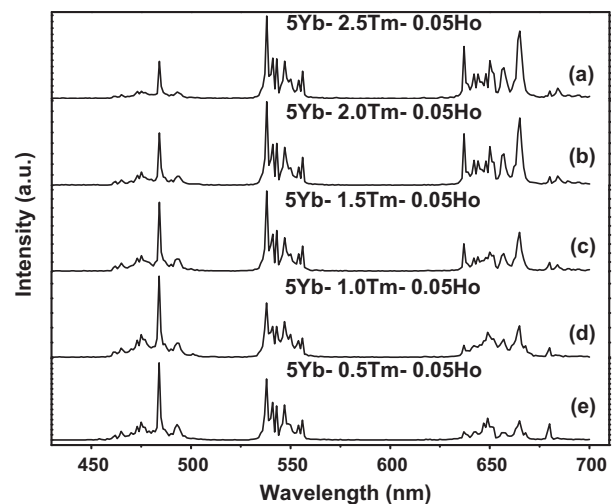


Fig. 5. Up-converted emission spectra of 5 at.%  $\text{Yb}^{3+}$ , 0.05 at.%  $\text{Ho}^{3+}:\text{Gd}_3\text{Ga}_5\text{O}_{12}$  nano-crystals doped with: (a) 2.5 at.% (b) 2.0 at.% (c) 1.5 at.% (d) 1.0 at.% (e) 0.5 at.%  $\text{Tm}^{3+}$  ions under diode laser excitation at 971.5 nm with  $3.33 \text{ W/cm}^2$ .

up-conversion emission, while green and red emission via two-photon process, which could explain the tendency of color coordinates toward to blue region at high pump power. The variation of color coordinates in the 1931 CIE diagram indicated a possible way to tune the obtained color via the laser pump power.

The tunable red-green-blue mechanism was rooted in the nearly resonant cross relaxation process  $^1\text{G}_4(\text{Tm}) + ^5\text{I}_7(\text{Ho}) \rightarrow ^3\text{H}_5(\text{Tm}) + ^5\text{S}_2(\text{Ho})$ . There are several reasons responsible for the occurrence of the cross relaxation process: Firstly, the energy mismatch of  $135 \text{ cm}^{-1}$  can easily be dissipated by the phonons of  $\text{Gd}_3\text{Ga}_5\text{O}_{12}$  lattice ( $600 \text{ cm}^{-1}$ ) and allow this process to efficiently occur. Secondly, both the  $^1\text{G}_4(\text{Tm})$  and  $^5\text{I}_7(\text{Ho})$  states are meta-stable states, which have enough time to allow this process to occur. Thirdly, the rise time for the  $^5\text{S}_2(\text{Ho})$  is reduced as compared to that  $\text{Gd}_3\text{Ga}_5\text{O}_{12}:\text{Yb}^{3+}/\text{Ho}^{3+}$  nano-crystals because the lifetime of  $^5\text{I}_7(\text{Ho})$  ( $\sim 817 \mu\text{s}$ ) state is longer than that of  $^1\text{G}_4(\text{Tm})$  ( $550 \mu\text{s}$ ) state. All facts have been identified by spectral and kinetic investigations, suggesting the occurrence of the proposed cross relaxation process.

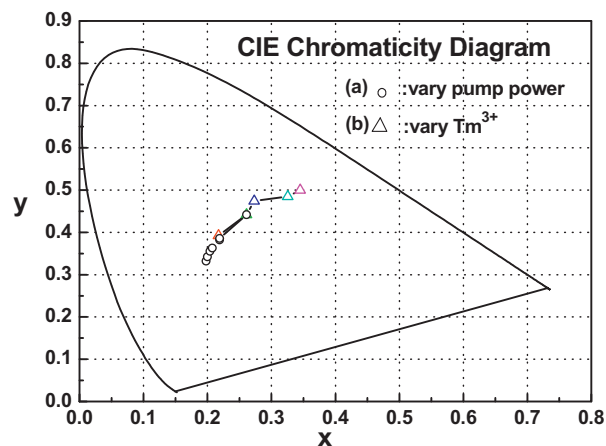
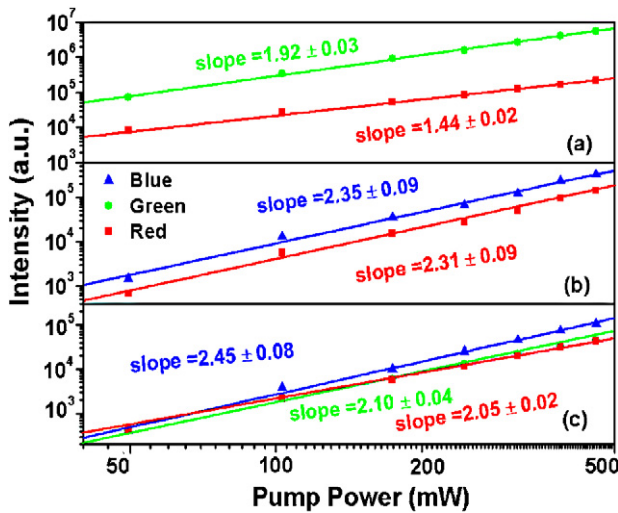


Fig. 6. Calculated 1931 CIE color coordinates for the blue, green and red UC luminescence of  $\text{Gd}_3\text{Ga}_5\text{O}_{12}$  nanocrystals doped with: (a)  $\circ$ : 5 at.%  $\text{Yb}^{3+}$ , 1 at.%  $\text{Tm}^{3+}$  and 0.05 at.%  $\text{Ho}^{3+}$  ions under diode laser excitation at 971.5 nm with various pump powers [ $6.87 \text{ W/cm}^2$  (right)– $30.5 \text{ W/cm}^2$  (left)]; (b)  $\triangle$ : 5 at.%  $\text{Yb}^{3+}$ ,  $z$  at.%  $\text{Tm}^{3+}$  and 0.05 at.%  $\text{Ho}^{3+}$  ions [ $y=0.5$  (left), 1.0, 1.5, 2.0, and 2.5 (right)] under diode laser excitation at 971.5 nm with  $3.33 \text{ W/cm}^2$ . (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)



**Fig. 7.** Pump power dependence of the blue, green and red up-converted emissions in  $\text{Ga}_3\text{Gd}_5\text{O}_{12}$  nanocrystals doped with (a) 5 at.%  $\text{Yb}^{3+}$  and 0.05 at.%  $\text{Ho}^{3+}$ , (b) 5 at.%  $\text{Yb}^{3+}$  and 1.0 at.%  $\text{Tm}^{3+}$ , (c) 5 at.%  $\text{Yb}^{3+}$ , 1 at.%  $\text{Tm}^{3+}$  and 0.05 at.%  $\text{Ho}^{3+}$  ions under diode laser excitation at 971.5 nm.

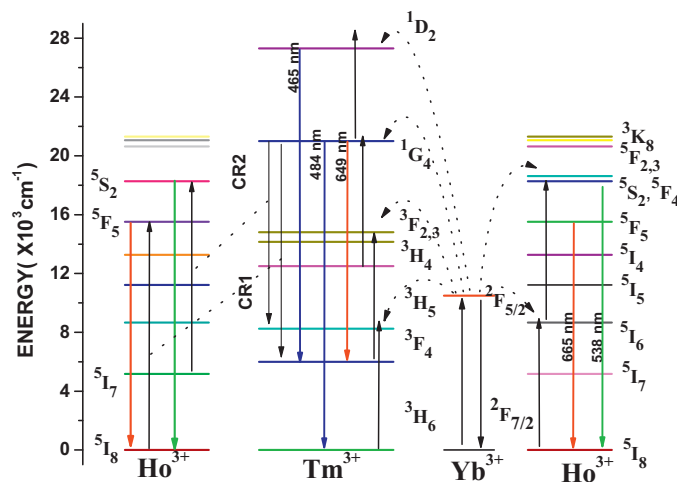
To better understand the up-conversion mechanism, the pump power dependence of the up-conversion emissions was investigated. The numbers of photons  $n$  can be calculated by the following equation [18]:

$$I \propto P^n \quad (2)$$

where  $I$  is the intensity of the fluorescence,  $P$  is the pump power,  $n$  is the number of photons required for populating the emitting state.

Fig. 7 shows three- and/or two-photon processes that involved producing the blue, green and red up-conversion emissions and similar to other  $\text{Yb}^{3+}/\text{Tm}^{3+}$  and  $\text{Yb}^{3+}/\text{Ho}^{3+}$  doped systems, respectively [15–17]. Unexpectedly, the slopes ( $n$ ) were smaller than the expected values, which can be attributed to the competition between linear decay and up-conversion processes for the depletion of the intermediate excited states [19].

Fig. 8 shows the schematic energy level diagram for the  $\text{Ho}^{3+}$ ,  $\text{Tm}^{3+}$  and  $\text{Yb}^{3+}$  ions as well as the proposed up-conversion mechanisms to produce the blue, green, and red up-conversion emissions.



**Fig. 8.** Schematic representation of the energy level diagram for the  $\text{Ho}^{3+}$ ,  $\text{Tm}^{3+}$  and  $\text{Yb}^{3+}$  ions as well as the proposed up-conversion mechanisms to produce the blue, green, and red up-converted emissions. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.)

The blue up-conversion emission arose from  $\text{Yb}^{3+}/\text{Tm}^{3+}$  pairs mainly via a well-known three-photon process, and the green band from  $\text{Yb}^{3+}/\text{Ho}^{3+}$  pairs was a two-photon process.

The difference between  $n$  values of blue up-conversion bands in Fig. 7b and c was not distinct except that a little difference which can be attributed to the experimental error. The phenomena indicated that blue up-conversion emission came from  $\text{Tm}^{3+}$  ions exclusively. The  $n$  value of the red up-conversion bands was 2.05 in Fig. 7c between  $\text{Ho}^{3+}$  and  $\text{Tm}^{3+}$  ions and 2.31 (Fig. 7b), indicating the fact that both  $\text{Ho}^{3+}$  and  $\text{Tm}^{3+}$  ions were responsible for the red up-conversion bands. Here, the red up-conversion bands arose from  $\text{Yb}^{3+}/\text{Tm}^{3+}$  and  $\text{Yb}^{3+}/\text{Ho}^{3+}$  pairs involving a mixed three/two-photon processes. The significantly variance of the  $n$  value for the red up-conversion bands may also support the occurrence of the CR1. It should be noted that the green up-conversion emission came from  $\text{Ho}^{3+}$  ions exclusively, because only  $\text{Ho}^{3+}$  ions contributed to the green up-conversion emission. Remarkably, the increased  $n$  value from 1.92 (Fig. 7a) to 2.10 (Fig. 7c) indicated that another mechanism happens involving a three-photon process to populate the  $^5\text{S}_2$  ( $\text{Ho}$ ) state, which is no other than the nearly resonant cross relaxation process of CR2:  $^1\text{G}_4$  ( $\text{Tm}$ ) +  $^5\text{I}_7$  ( $\text{Ho}$ )  $\rightarrow$   $^3\text{H}_5$  ( $\text{Tm}$ ) +  $^5\text{S}_2$  ( $\text{Ho}$ ). This resonant cross relaxation process also supported the mixed three/two-photon processes for the red up-conversion emission.

#### 4. Conclusion

In summary, rare-earth-ion doped  $\text{Gd}_3\text{Ga}_5\text{O}_{12}$  phosphors have been successfully prepared via a citric acid complex procedure. The red-green-blue up-conversion luminescence was achieved in  $\text{Gd}_3\text{Ga}_5\text{O}_{12}:\text{Yb}^{3+}/\text{Tm}^{3+}/\text{Ho}^{3+}$  nano-crystals excited with 971.5 nm LD and the up-conversion processes were discussed. Results indicated that the multi-colors of the  $\text{Gd}_3\text{Ga}_5\text{O}_{12}:\text{Yb}^{3+}/\text{Tm}^{3+}/\text{Ho}^{3+}$  nano-crystals could be adjusted by changing the doped concentrations of  $\text{Tm}^{3+}$  ions. The intensity ratio of red-green-blue could be tuned to be almost 1:1:1 when the doped concentrations of  $\text{Yb}^{3+}$ ,  $\text{Tm}^{3+}$  and  $\text{Ho}^{3+}$  were 5 at.%, 2.0 at.% and 0.05 at.%. In the complex tri-doped energy transfer systems, the mechanism was complex. We found that the red up-conversion transfer from  $\text{Tm}^{3+}$  to  $\text{Ho}^{3+}$  ions was based on the nearly resonant cross relaxation process  $^1\text{G}_4$  ( $\text{Tm}$ ) +  $^5\text{I}_8$  ( $\text{Ho}$ )  $\rightarrow$   $^3\text{F}_4$  ( $\text{Tm}$ ) +  $^5\text{F}_5$  ( $\text{Ho}$ ). The three-photon nearly resonant cross relaxation process enhanced the green and red up-conversion emissions. Obviously, the  $\text{Gd}_3\text{Ga}_5\text{O}_{12}:\text{Yb}^{3+}/\text{Tm}^{3+}/\text{Ho}^{3+}$  nano-crystals could have potential application in the fields of lighting, displays and photonics.

#### Acknowledgements

This research was supported by National Nature Science Foundation of China (nos. 50902129, 61078076), Major Projects from FJIRSM (SZD09001), Knowledge Innovation Program of the Chinese Academy of Sciences (KJXC2-EW-H03), Fund of Key Laboratory of Optoelectronic Materials Chemistry and Physics and Chinese Academy of Sciences (2008DP173016), Science and Technology Plan Major Project of Fujian Province of China (grant no. 2010I0015) and Fund of Research Center of Laser Technology Integration and Application Engineering Technology of Haixi Industrial Technology Research Institute (2009H2009).

#### References

- [1] X.F. Yu, M. Li, M.Y. Xie, L.D. Chen, Y. Li, Q.Q. Wang, Nano Res. 3 (2010) 51–60.
- [2] F. Zhang, D.Y. Zhao, Nano Res. 2 (2009) 292–305.
- [3] Y.G. Chen, Y. Liu, Y.G. Zhang, G. Somesfalean, Z.G. Zhang, Q. Sun, F.P. Wang, Appl. Phys. Lett. 91 (2007) 133103–133106.

- [4] L. Cheng, K. Yang, S. Zhang, M.W. Shao, S.T. Lee, Z. Liu, *Nano Res.* 3 (2010) 722–732.
- [5] L. Gao, X. Ge, Z.L. Chai, G.H. Xu, X. Wang, C. Wang, *Nano Res.* 2 (2009) 565–574.
- [6] H.X. He, Y.M. Guan, Y.C. Zhang, *J. Alloys Compd.* 509 (2011) 341–343.
- [7] G.S.R. Raju, J.Y. Park, H.C. Jung, E. Pavitra, B.K. Moon, J.H. Jeong, J.S. Yu, J.H. Kim, H.Y. Choi, *J. Alloys Compd.* 509 (2011) 7537–7542.
- [8] Y.H. Liu, W.D. Zhuang, Y.S. Hu, W.G. Gao, *J. Alloys Compd.* 504 (2011) 488–492.
- [9] J. Chen, X.H. Gong, Y.F. Lin, Y.J. Chen, Z.D. Luo, Y.D. Huang, *J. Alloys Compd.* 492 (2011) 667–670.
- [10] A.S. Gouveia-Neto, L.A. Bueno, R.F. do Nascimento Jr., E.A. da Silva, E.B. da Costa, V.B. do Nascimento, *Appl. Phys. Lett.* 91 (2007) 091114.
- [11] N.K. Giri, D.K. Rai, S.B. Rai, *Appl. Phys. B: Laser Optical* 91 (2008) 437.
- [12] R. Naccache, F. Vetrone, J.C. Boyer, J.A. Capobianco, A. Speghini, M. Bettinelli, *J. Nanosci. Nanotechnol.* 4 (2004) 1025.
- [13] S. Biamino, C. Badini, *J. Eur. Ceram. Soc.* 24 (2004) 3021.
- [14] R. Krsmanovic, S. Polizzi, P. Canton, *Mater. Sci. Forum.* 494 (2005) 143.
- [15] D.Q. Chen, Y.S. Wang, Y.L. Yu, P. Huang, *Appl. Phys. Lett.* 91 (2007) 051920–51923.
- [16] F. Pandozzi, F. Vetrone, J.C. Boyer, R. Naccache, J.A. Capobianco, A. Speghini, M. Bettinelli, *J. Phys. Chem. B* 109 (2005) 17400.
- [17] J.C. Boyer, F. Vetrone, J.A. Capobianco, A. Speghini, M. Bettinelli, *Chem. Phys. Lett.* 390 (2004) 403.
- [18] M. Pollnau, D.R. Gamelin, S.R. Luthi, H.U. Güdel, M.P. Hehlen, *Phys. Rev. B* 61 (2000) 3337.
- [19] A. Brenier, C. Madej, C. Pédrini, G. Boulon, *Radiat. Eff. Defects Solids* 135 (1995) 73.