Highly efficient red upconversion fluorescence emission in $\text{Yb}^{3+}/\text{Ho}^{3+}/\text{Ce}^{3+}$ codoped LaF_3 nanocrystals

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Abstract

The $\text{Yb}^{3+}/\text{Ho}^{3+}/\text{Ce}^{3+}$ codoped LaF_3 nanocrystals have been successfully prepared via a facile hydrothermal method. The significant enhancement in the red upconversion emission of Ho^{3+} is successfully obtained in $\text{LaF}_3:\text{Yb}^{3+}/\text{Ho}^{3+}$ nanocrystals through introducing of Ce^{3+} under NIR excitation at 980 nm. The red-to-green emission ratio of Ho^{3+} is enhanced 18.9-fold with Ce^{3+} concentration increasing to 12%, which is due to the two efficient cross relaxation processes of $^5\text{I}_6 (\text{Ho}^{3+}) + ^2\text{F}_{5/2} (\text{Ce}^{3+}) \rightarrow ^5\text{I}_7 (\text{Ho}^{3+}) + ^2\text{F}_{7/2} (\text{Ce}^{3+})$ and $^5\text{S}_2/^5\text{F}_4 (\text{Ho}^{3+}) + ^2\text{F}_{5/2} (\text{Ce}^{3+}) \rightarrow ^5\text{F}_5 (\text{Ho}^{3+}) + ^2\text{F}_{7/2} (\text{Ce}^{3+})$ between Ho^{3+} and Ce^{3+} ions. The enhancement mechanism of red emission and conversion efficiency between Ho^{3+} and Ce^{3+} are investigated in detail.

Keywords: $\text{LaF}_3:\text{Yb}^{3+}/\text{Ho}^{3+}$ nanocrystals, Upconversion luminescence, Cross relaxation

1. Introduction

Rare-earth(RE)-doped upconversion (UC) fluoride nanomaterials have been widely applied in phosphor, color display, optical storage, solid-state laser, solar cell and biomedical imaging, which because of low phonon energies, high radiative emission rate and high chemical stability[1-6]. Up to now, the different morphologies, sizes, structures and fluorescence properties of fluoride nanomaterials, such as LaF_3 , NaYF_4 , NaLuF_4 and LiYF_4 have been successfully synthesized by different methods[7-10]. And these RE-doped nanomaterials display multipeak emission profiles. Meanwhile, there are many methods to tune UC emission in fluoride nanocrystals(NCs), especially obtained red UC emission [11-13]. In fact, it is difficult to obtain single red UC emission in fluoride NCs, which due to the abundance radiative and non-radiative transition channel of $4f^N$ electronic states of RE ions. Therefore, achieving high-purity single red UC emission has been an increasing focus and challenge. Recently, several researchers have attempted to get a single-band red UC emission by codoping ions or building composite structure. For example, the strong single-band red UC emission was obtained in $\text{NaYF}_4:\text{Yb}^{3+}/\text{Er}^{3+}$ crystals by increasing Yb^{3+} concentration, introducing Mn^{2+} , Pb^{2+} ions or attaching gold nanoparticles(Au NPs), etc.[14-17]. Zhang's group has reported that the UC emission of Ho^{3+} was changed from green to red in cubic phase $\text{NaYF}_4:\text{Yb}^{3+}/\text{Ho}^{3+}$ NCs by introducing Ce^{3+} [18]. However, few reports have been found on the single-band red UC emission of Ho^{3+} in $\text{LaF}_3:\text{Yb}^{3+}/\text{Ho}^{3+}$ NCs by codoping RE ions. The enhancement of red emission from Yb^{3+} and Ho^{3+} codoped LaF_3 nanoparticles embedded in a silica matrix can be achieved by careful tuning of the sol-gel process[19].

In the present work, the $\text{LaF}_3:\text{Yb}^{3+}/\text{Ho}^{3+}$ NCs with codoping Ce^{3+} ions have been synthesized using a facile hydrothermal method. The phase and morphology of $\text{LaF}_3:\text{Yb}^{3+}/\text{Ho}^{3+}$ NCs are characterized and confirmed by XRD and TEM. A confocal setup with different excitation lights have been carried out to explore the UC emission properties and energy transfer (ET) process. The possible upconversion mechanism and conversion efficiency of Ho^{3+} and Ce^{3+} in LaF_3 NCs are investigated in detail.

2. Experimental details

2.1. Sample preparation

All chemicals used in the current study were analytical graded used without further purification. (La_2O_3 :44%) were supplied by Sinopharm Chemical Reagent Co., Ltd. $\text{Yb}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ and $\text{Ho}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ are obtained by dissolving Ho_2O_3 , and Yb_2O_3 (99.99%, Sigma-Aldrich Chemicals Co.) in dilute nitric acid solution at elevated temperature followed by evaporating the superfluous nitric acid, respectively. $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (99.99%) was directly purchased from Sigma-Aldrich Chemicals Co.. NH_4F (Sodium fluoride, 98.0%) with analytical grade were supplied by the Tianjin chemical reagent factory.

A series of $\text{LaF}_3:\text{Yb}^{3+}/\text{Ho}^{3+}$ NCs with codoping different Ce^{3+} concentration were synthesized by a facile hydrothermal method[20]. The detailed process is given in the reference. Typically, (0.39- x) ml $\text{La}(\text{NO}_3)_3$ (0.50M), 0.10 ml $\text{Yb}(\text{NO}_3)_3$ (0.50M) 0.01 ml $\text{Ho}(\text{NO}_3)_3$ (0.50M), x ml ($x=0, 0.02, 0.03, 0.04, 0.05, 0.06$) $\text{Ce}(\text{NO}_3)_3$ (0.50M) and 0.35ml NH_4F (0.20M) were added to the solution and stirred for 30 min. The resulting solution was transferred to a 40 mL Telfon-lined autoclave, and heated at 180 °C for 7

h. Finally, LaF_3 : 20% Yb^{3+} /2% Ho^{3+} / $x\%$ Ce^{3+} NCs were collected by centrifuging and washing with deionized water and ethanol three times, respectively. The collected LaF_3 NCs were obtained and dried at 60°C for 12 h.

2.2. Characterization

The powder x-ray diffraction (XRD) patterns are recorded by D/Max2550VB+/PCx-ray diffraction meter with $\text{Cu K}\alpha$ (40 kV, 40 mA) irradiation ($\lambda = 0.15406$ nm). The 2θ angle of the XRD spectra recorded at a scanning rate of 8° min^{-1} . The morphology of the particles was characterized by the transmission electron microscope (TEM, JEM 2100). For spectroscopic measurements, YAG: Nd^{3+} (Quanta Ray Lab-170, 10Hz, 532 nm) pulse laser and Ti sapphire laser (MRB-110, 700-1000 nm) are employed as excitation sources. The spectrometer (SP2750i) with a spectral resolution of 0.008 nm is used for luminescence collection and detection. The optical microscope (OLYMPUS-BX51) is used in the confocal setup. All of the spectroscopic measurements are carried out at room temperature.

3 Results and discussion

3.1. XRD and TEM.

The crystal structure and phase purity of LaF_3 : 20% Yb^{3+} /2% Ho^{3+} NCs with codoping different Ce^{3+} concentration are confirmed by XRD, as shown in Fig.1. All the diffraction peaks from LaF_3 NCs coincides well with the standard pattern of JCPDS 32-0483, which indexes to pure hexagonal phase LaF_3 . No obvious extra diffraction peaks were detected even with increasing Ce^{3+} concentration from 0% to 12%. The TEM images of the LaF_3 : Yb^{3+} / Ho^{3+} NCs codoped 0-12mol% Ce^{3+} are

shown in Fig.2. A series of Ce^{3+} -doped $\text{LaF}_3:\text{Yb}^{3+}/\text{Ho}^{3+}$ NCs are monodisperse nanorods with an average diameter of 10 nm and a length of 20 nm. It is found that the crystal phase, morphology and size of $\text{LaF}_3:\text{Yb}^{3+}/\text{Ho}^{3+}$ NCs has no obvious effect with increasing Ce^{3+} concentration in Fig. 1 and Fig. 2, which may be due to the very close ionic radius between Ce^{3+} ($r=0.128$ nm) and La^{3+} ($r=0.130$ nm) [21-22].

3.2 Photoluminescence study

3.3.1 UC emission

The UC emission of $\text{LaF}_3:\text{Yb}^{3+}/\text{Ho}^{3+}$ NCs is studied by a confocal microscope setup. Fig. 3 shows the UC emission spectra, the red-to-green (R/G) emission ratio, the peak area of green and red emission and the Commission Internationale del'Eclairage (CIE) 1931 (x, y) chromaticity coordinates of $\text{LaF}_3:\text{Yb}^{3+}/\text{Ho}^{3+}$ NCs with increasing Ce^{3+} ion concentration from 0% to 12% under NIR 980 nm excitation, together with their luminescence photographs. The strong green UC emission and accompanying with red UC emission is observed in Fig.3a, which can be assigned to the transitions of $^5\text{S}_2/^5\text{F}_4 \rightarrow ^5\text{I}_8$ (center at 540 nm) and $^5\text{F}_5 \rightarrow ^5\text{I}_8$ (center at 650 nm), respectively[24]. And some weak blue and NIR emissions can be also found, which are associated with the transitions of $^5\text{F}_3 \rightarrow ^5\text{I}_8$ (center at 484nm) and $^5\text{S}_2/^5\text{F}_4 \rightarrow ^5\text{I}_7$ (center at 750 nm)[24]. It is interesting to observe that the red UC emission intensity increases with the green emission intensity decreases when the concentration of Ce^{3+} increasing from 0% to 12%. And the luminescent colors from $\text{LaF}_3:\text{Yb}^{3+}/\text{Ho}^{3+}$ NCs can be tuned from green to red is shown in the inset of Fig.3a. According to the Fig. 3b, it is found that the R/G ratio increases from 0.52 to 9.83.

The peak area of red UC emission evidently increases with Ce^{3+} concentration increasing as shown in Fig. 3c. The corresponding CIE chromaticity coordinate (x , y) can be calculated according to the UC emission spectra is listed in the Table 1. Note that CIE chromaticity coordinate (x , y) is tuned from (0.3197, 0.6078) to (0.5392, 0.3403) with Ce^{3+} concentrations increasing from 0% to 12.0% as shown in Fig.3d. This result further indicates that the luminescent color of $\text{LaF}_3:\text{Yb}^{3+}/\text{Ho}^{3+}$ NCs is changed from green region to red region.

3.2.2 UC mechanism

To understand the observed phenomenon, the green and red UC emission mechanisms are firstly studied. For the UC emission mechanism, the number of photons required to populate the upper emitting state under unsaturated condition can be described by the following relationship: $I_{up} \propto P^n$, where I_{up} is the UC luminescence intensity, P is the infrared excitation pump power, and n is the number of pump photons required[24]. Fig. 4 shows the Log–Log plot of the green and red UC emission intensities as a function of the infrared excitation pump power for $\text{LaF}_3:\text{Yb}^{3+}/\text{Ho}^{3+}$ NCs ($x=0\%$ (a) and 12% (b)). The Log–Log plot can be yield a straight line with slope n . Slopes of n for green and red emissions from $\text{LaF}_3:20\%\text{Yb}^{3+}/2\%\text{Ho}^{3+}$ and $\text{LaF}_3:20\%\text{Yb}^{3+}/2\%\text{Ho}^{3+}/12\%\text{Ce}^{3+}$ NCs are close to 2 in Fig. 3, which indicates that the green and red UC emissions are all two photon excitation processes[26]. Noticed that the slopes of n from $\text{LaF}_3:20\%\text{Yb}^{3+}/2\%\text{Ho}^{3+}/12\%\text{Ce}^{3+}$ NCs are slightly smaller than that $\text{LaF}_3:20\%\text{Yb}^{3+}/2\%\text{Ho}^{3+}$ NCs, which was mainly attributed to the change of population of intermediate level of the red due to the

quenching of the green UC emissions[24].

To further explore different UC emission spectrum phenomenon of Ho^{3+} in $\text{LaF}_3:20\%\text{Yb}^{3+}/2\%\text{Ho}^{3+}$ NCs arise from the influence of Ce^{3+} . The main processes of radiative transition and ET for UC emission in LaF_3 NCs can be discussed based on the UC emission spectra. Fig. 5 illustrates a scheme of the possible UC emission processes of $\text{Yb}^{3+}/\text{Ho}^{3+}/\text{Ce}^{3+}$ systems[25]. The main pathways to populate upper emitting states are through the ET from Yb^{3+} to Ho^{3+} , which due to Yb^{3+} has a larger absorption cross-section for infrared light and longer lifetime than Ho^{3+} . Under NIR 980 nm excitation, the excited state $^5\text{I}_6$, $^5\text{F}_5$ and $^5\text{S}_2/^5\text{F}_4$ of Ho^{3+} can be populated by ET processes from neighboring Yb^{3+} . When the excited state $^5\text{S}_2/^5\text{F}_4$ and $^5\text{F}_5$ radiative decay to the ground state $^5\text{I}_8$, the green and red UC emission can be achieved according to Fig.4. It is found that the red UC emission mainly originate from excited state $^5\text{F}_5$. The two possible transition processes could populate the excited state $^5\text{F}_5$ level. One is the direct population from the nonradiative transition from higher excited state of $^5\text{F}_4/^5\text{S}_2$. The other is from $^5\text{I}_7$ to $^5\text{F}_5$ state state by through the ET process from Yb^{3+} to Ho^{3+} , and $^5\text{I}_7$ state can be populated through the nonradiative relaxation of the $^5\text{I}_6$ state. This result indicates that the nonradiative relaxation processes from $^5\text{S}_2/^5\text{F}_4 \rightarrow ^5\text{F}_5$ and $^5\text{I}_6 \rightarrow ^5\text{I}_7$ is very important for the red UC emission in $\text{LaF}_3:20\%\text{Yb}^{3+}/2\%\text{Ho}^{3+}$ NCs. As is well known, the rate of nonradiative relaxation of multiphonon relaxation (MR) in the RE ions can be expressed as[26],

$$W_{NR} \propto \exp^{-aP} \quad (1)$$

where, a is the host constants, $P=\Delta E/h\nu$ is the number of phonons involved, ΔE is

the energy gap between two energy levels; and $h\nu$ is the phonon energy of the host. Generally, the nonradiative MR process dominates over radiative process when the P is less than 5. The maximum phonon energy of LaF_3 is about 355 cm^{-1} is approximately eight times smaller than both energy gaps are about 3000 cm^{-1} of $^5\text{S}_2/^5\text{F}_4 \rightarrow ^5\text{F}_5$ and $^5\text{I}_6 \rightarrow ^5\text{I}_7$ states. Therefore, the two nonradiative relaxation processes originate from $^5\text{S}_2/^5\text{F}_4 \rightarrow ^5\text{F}_5$ and $^5\text{I}_6 \rightarrow ^5\text{I}_7$ states are no efficient [27]. However, when Ce^{3+} is doped to the $\text{Yb}^{3+}/\text{Ho}^{3+}$ system, different UC emission phenomena are observed as shown in Fig. 3. When Ce^{3+} concentration is increased to 12% in LaF_3 : 20% $\text{Yb}^{3+}/2\% \text{Ho}^{3+}$ NCs, one can clearly find that the color of fluorescence emission of Ho^{3+} is tuned from green to red. Since the energy gap of Ce^{3+} ions between the excited $^5\text{F}_{7/2}$ state and ground $^2\text{F}_{5/2}$ state is about 3000 cm^{-1} is similar to the gaps of $^5\text{S}_2/^5\text{F}_4 \rightarrow ^5\text{F}_5$ and $^5\text{I}_6 \rightarrow ^5\text{I}_7$ states of Ho^{3+} [28], the CR processes of $^5\text{S}_2(^5\text{F}_4) (\text{Ho}^{3+}) + ^2\text{F}_{5/2} (\text{Ce}^{3+}) \rightarrow ^5\text{F}_5 (\text{Ho}^{3+}) + ^2\text{F}_{7/2} (\text{Ce}^{3+})$ and $^5\text{I}_6 (\text{Ho}^{3+}) + ^2\text{F}_{5/2} (\text{Ce}^{3+}) \rightarrow ^5\text{I}_7 (\text{Ho}^{3+}) + ^2\text{F}_{7/2} (\text{Ce}^{3+})$ can be effectively achieved according to the energy conservation law. These resonant energy transfer processes can increase the population of $^5\text{F}_5$ state through nonradiative transitions of $^5\text{S}_2/^5\text{F}_4 \rightarrow ^5\text{F}_5$ and $^5\text{I}_6 \rightarrow ^5\text{I}_7$, respectively, which leads to the enhancement of red emission and the suppress of green emission.

Fig. 6 shows NIR emission of $^5\text{I}_6 \rightarrow ^5\text{I}_8$ transition of LaF_3 : $\text{Yb}^{3+}/\text{Ho}^{3+}$ NCs with codoping different Ce^{3+} concentrations under NIR 980 nm excitation. Noticed that the emission intensity of NIR quickly decreases with the increase of Ce^{3+} concentration from 0% to 12%. To the best of our knowledge, the fluorescence emission intensity mainly ascribes to the competition between radiative relaxation and non-radiative

relaxation. The intensity of NIR emission decreases indicates that nonradiative decay rate from 5I_6 state have been increased. This further confirms the occurrence of CR1 process $^5I_6(\text{Ho}^{3+}) + ^2F_{5/2}(\text{Ce}^{3+}) \rightarrow ^5I_7(\text{Ho}^{3+}) + ^2F_{7/2}(\text{Ce}^{3+})$ between Ho^{3+} and Ce^{3+} .

Fig. 7 shows the downconversion (DC) emission, R/G ratio and the peak area of green and red UC emission in $\text{LaF}_3: \text{Yb}^{3+}/\text{Ho}^{3+}$ NCs with the increase of Ce^{3+} concentration under 532 nm pulsed laser excitation. With the Ce^{3+} concentration is increased, the green UC emission intensity reduces and red UC emission increases, the corresponding R/G ratio increases from 0.24 to 0.81. The $^5S_2/^5F_4$ excited state can be directly populated by 532 nm pulsed laser according to Fig. 4, and the green emission is achieved by radiative decay from $^5S_2/^5F_4 \rightarrow ^5I_8$ state. The red emission mainly originates from 5F_5 state. However, the population of 5F_5 state mainly depends on $^5S_2/^5F_4$ excited states through nonradiative relaxation. Thus, the increase of red emission intensity can be used to confirm the occurrence of CR2 processes $^5S_2/^5F_4(\text{Ho}^{3+}) + ^2F_{5/2}(\text{Ce}^{3+}) \rightarrow ^5F_5(\text{Ho}^{3+}) + ^2F_{7/2}(\text{Ce}^{3+})$ between Ho^{3+} and Ce^{3+} .

3.2.3 The conversion efficiency of CR 1 and CR 2 processes

The conversion efficiency of CR1 and CR2 processes between Ho^{3+} and Ce^{3+} can be calculated based on the steady-state rate equation and decay lifetime. According to the proposed ET UC process of Yb^{3+} - Ho^{3+} - Ce^{3+} codoped system, the corresponding rate equations of ET are established. $n_{\text{Ho},0}$, $n_{\text{Ho},1}$, $n_{\text{Ho},2}$, $n_{\text{Ho},3}$ and $n_{\text{Ho},4}$ represent the population densities of the 5I_8 , 5I_7 , 5I_6 , 5F_5 and $^5S_2(^5F_4)$ states of the Ho^{3+} , respectively. $n_{\text{Yb},0}$ and $n_{\text{Yb},1}$ refer to the population densities of the $^2F_{7/2}$ and $^2F_{5/2}$ states of the Yb^{3+} ions. $n_{\text{Ce},0}$ and $n_{\text{Ce},1}$ are the population densities of the $^2F_{5/2}$ and $^2F_{7/2}$ states

of the Ce^{3+} . k_0 , k_1 and k_2 are ET rates from Yb^{3+} to Ho^{3+} , $n_{\text{Yb},1}$ to $n_{\text{Yb},0}$ and n_0 to n_2 , $n_{\text{Yb},1}$ to $n_{\text{Yb},0}$ and $n_{\text{Ho},1}$ to $n_{\text{Ho},3}$, $n_{\text{Yb},1}$ to $n_{\text{Yb},0}$ and $n_{\text{Ho},2}$ to $n_{\text{Ho},4}$, respectively; R_1 , R_2 , R_3 and R_4 are the radiation rates of the $^5\text{I}_7 \rightarrow ^5\text{I}_8$, $^5\text{I}_6 \rightarrow ^5\text{I}_8$, $^5\text{F}_5 \rightarrow ^5\text{I}_8$ and $^5\text{S}_2(^5\text{F}_4) \rightarrow ^5\text{I}_8$ states of Ho^{3+} , respectively; β_0 and β_2 refer to nonradiative decay rates from $^5\text{I}_6 \rightarrow ^5\text{I}_7$ and $^5\text{S}_2/^5\text{F}_4 \rightarrow ^5\text{F}_5$ states, respectively; r_1 and r_2 represent the Ho^{3+} to Ce^{3+} CR processes [$^5\text{I}_6 (\text{Ho}^{3+}) + ^2\text{F}_{5/2} (\text{Ce}^{3+}) \rightarrow ^5\text{I}_7 (\text{Ho}^{3+}) + ^2\text{F}_{7/2} (\text{Ce}^{3+})$ and $^5\text{S}_2/^5\text{F}_4 (\text{Ho}^{3+}) + ^2\text{F}_{5/2} (\text{Ce}^{3+}) \rightarrow ^5\text{F}_5 (\text{Ho}^{3+}) + ^2\text{F}_{7/2} (\text{Ce}^{3+})$], respectively. Considering that energy gaps between $^5\text{I}_4$ and $^5\text{I}_6$ states and between $^5\text{I}_5$ and $^5\text{I}_6$ states are small, which results in very small radiation rates according to Fig. 4. Thus, their radiation rates can be neglected in rate equations. The rate equations of each energy state are formulated as follows[18,29]:

$$\beta_0 n_{\text{Ho},2} + r_1 n_{\text{Ho},2} n_{\text{Ce},0} - R_1 n_{\text{Ho},1} - k_1 n_{\text{Yb},1} n_{\text{Ho},1} = 0 \quad (2a)$$

$$k_0 n_{\text{Yb},1} n_{\text{Ho},0} - \beta_0 n_{\text{Ho},2} - r_1 n_{\text{Ho},2} n_{\text{Ce},0} - R_2 n_{\text{Ho},2} - k_2 n_{\text{Yb},1} n_{\text{Ho},1} = 0 \quad (2b)$$

$$k_1 n_{\text{Yb},1} n_{\text{Ho},1} + r_2 n_{\text{Ho},4} n_{\text{Ce},0} + \beta_1 n_{\text{Ho},4} - R_3 n_{\text{Ho},3} = 0 \quad (2c)$$

$$k_2 n_{\text{Yb},1} n_{\text{Ho},2} - R_4 n_{\text{Ho},4} - r_2 n_{\text{Ho},4} n_{\text{Ce},0} - \beta_1 n_{\text{Ho},4} = 0 \quad (2d)$$

Generally, the intrinsic decay rates in the intermediate states are much larger than the UC energy transfer rates[25]. Thus, one can estimate the emission intensity of NIR ($^5\text{I}_6 \rightarrow ^5\text{I}_8$) by solving equations (2a-2d), which is:

$$I_{\text{NIR}} = n_{\text{Ho},2} h\nu_{\text{NIR}} R_2 = \frac{R_2}{R_2 + r_1 n_{\text{Ce},0}} h\nu_{\text{NIR}} k_0 n_{\text{Ho},0} n_{\text{Yb},1} \quad (3)$$

Based on the measured fluorescence intensity in Fig. 6 and equation (3), we have

$$\frac{I_{\text{NIR}}(0\% \text{Ce})}{I_{\text{NIR}}(12.0\% \text{Ce})} = \frac{R_2 + r_1 n_{\text{Ce},0}}{R_2} = 1 + \frac{r_1 n_{\text{Ce},0}}{R_2} = 6.2 \quad (4)$$

Thus, the conversion efficiency of the CR1 process[18]:

$$\eta_1 = \frac{\beta + r_1 n_{Ce,0}}{R_2 + r_1 n_{Ce,0}} \approx \frac{r_1 n_{Ce,0}}{R_2 + r_1 n_{Ce,0}} = 84.1\% \quad (5)$$

The conversion efficiency of CR2 process can be calculated by following equation[30]:

$$\eta_2 = 1 - \frac{\tau(12\%Ce)}{\tau'(0\%Ce)} = 32.9\% \quad (6)$$

The fluorescence decay times are measured to be about 98.2 μ s and 65.9 μ s for codoping 0% and 12% Ce^{3+} ions, respectively, as shown in Fig 7. According to above discussions and results which indicates that CR2 plays an assistant role for CR1 process in converting the green UC emission into red UC emission.

4. Conclusion

The pure hexagonal phase $LaF_3:Yb^{3+}/Ho^{3+}$ NCs with codoping different Ce^{3+} have been successfully synthesized by hydrothermal method. The strong red UC emission has been successfully obtained through increasing Ce^{3+} concentration under NIR 980nm excitation. The corresponding R/G ratio is increased from 0.52 to 9.83. The results indicate that two efficient CR processes between Ho^{3+} and Ce^{3+} are employed to increase the population of 5F_5 state, which leads to the enhancement of red emission and the suppress of green emission. The calculated conversion efficiency indicates that the strong red UC emission is mainly decided by CR1 process, and the CR2 process is an assistant role. The high-purity single red UC emission from $LaF_3:Yb^{3+}/Ho^{3+}/Ce^{3+}$ NCs will be useful for biological imaging and color display applications.

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Figure

Fig. 1. XRD patterns of LaF₃: 20%Yb³⁺/2%Ho³⁺ NCs with Ce³⁺ ions of 0%, 6%, 8% and 12%.

Fig. 2. SEM images of LaF₃: 20%Yb³⁺/2%Ho³⁺ NCs with Ce³⁺ ions of 0%, 6%, 8% and 12%.

Fig. 3. (a) UC emission spectra, (b) R/G ratio, (c) the peak area of the green and red

emission and (d) CIE chromaticity diagram of $\text{LaF}_3: 20\% \text{Yb}^{3+}/2\% \text{Ho}^{3+}$ NCs as a function of Ce^{3+} concentration. The inset is luminescence photographs.

Fig.4. Pump power dependences of $\text{LaF}_3: 20\% \text{Yb}^{3+}/2\% \text{Ho}^{3+}/x\% \text{Ce}^{3+}$ NCs ($x=0\%$ (a) and 12% (b)).

Fig. 5. Energy level diagrams of Ho^{3+} , Yb^{3+} and Ce^{3+} ions as well as proposed UC mechanism.

Fig. 6. The NIR emission spectra of $\text{LaF}_3: \text{Yb}^{3+}/\text{Ho}^{3+}$ NCs with different Ce^{3+}

concentrations under 980 nm excitation.

Fig. 7. (a) DC emission spectra, (b) R/G ratio and (c) the peak area of the green and red emission of $\text{LaF}_3: \text{Yb}^{3+}/\text{Ho}^{3+}$ NCs under pulse laser 532 nm excitation with different Ce^{3+} concentrations.

Fig. 8. DC luminescence decays of $^5\text{S}_2/^5\text{F}_4 \rightarrow ^5\text{I}_8$ transition at 541 nm of Ho^{3+} for $\text{NaLuF}_4: 20\% \text{Yb}^{3+}/2\% \text{Ho}^{3+}/x\text{Ce}^{3+}$ NCs ($x=0\%$ and 12%). The luminescence decay curves are fitted by using a single exponential function.

Table 1 The calculated CIE chromaticity coordinates (x , y) of $\text{LaF}_3\text{: Yb}^{3+}/\text{Ho}^{3+}$ NCs with different Ce^{3+} concentrations.

Point	Samples	CIE chromaticity coordinates	
		x	y
a	$\text{LaF}_3\text{: 20\% Yb}^{3+}/2\%\text{Ho}^{3+}$	0.3197	0.6078
b	$\text{LaF}_3\text{: 20\% Yb}^{3+}/2\%\text{Ho}^{3+}/4\%\text{Ce}^{3+}$	0.3721	0.5149
c	$\text{LaF}_3\text{: 20\% Yb}^{3+}/2\%\text{Ho}^{3+}/6\%\text{Ce}^{3+}$	0.4337	0.4683
d	$\text{LaF}_3\text{: 20\% Yb}^{3+}/2\%\text{Ho}^{3+}/8\%\text{Ce}^{3+}$	0.4801	0.4325
e	$\text{LaF}_3\text{: 20\% Yb}^{3+}/2\%\text{Ho}^{3+}/12\%\text{Ce}^{3+}$	0.5392	0.3403