Enhancement of red upconversion emission of cubic phase NaLuF₄: Yb³⁺/Ho³⁺/Ce³⁺ nanocrystals

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Abstract

The red upconversion emission of lanthanide-doped fluoride nanocrystals have great potential applications in color display and anticounterfeiting applications, especially for biological imaging and biomedical. In this work, a significant enhancement of red upconversion emission of Ho³⁺ ions was successfully obtained in the cubic phase NaLuF₄ nanocrystals through codoping Ce³⁺ ions under NIR 980 nm excitation. The ratio of red-to-green emission of Ho³⁺ ions was enhanced about 10-fold, which is due to two efficient cross relaxation processes derived from Ho³⁺ and Ce³⁺ ions promoted the red emission and quenched the green emission. The upconversion emission and luminescent colors of NaLuF₄: Yb³⁺/Ho³⁺ nanocrystals were carefully investigated by a confocal microscopy setup. The possible upconversion emission mechanism and conversion efficiency of cross relaxation between Ho³⁺ and Ce³⁺ ions were discussed in detail. The current study suggests that strong red emission of NaLuF₄: Yb³⁺/Ho³⁺/Ce³⁺ nanomaterials can be used for color display and anticounterfeiting techniques.

Keywords: A. optical materials; A. fluorides; C. transmission electron microscopy (TEM); D. optical properties; D. luminescence

1 Introduction

In recent years, lanthanide-doped upconversion (UC) fluoride materials have been widely applied in phosphors, color displays, optical storages, solid-state lasers, solar cells and biomedical imaging, which is due to the low phonon energy can effectively suppress nonradiative multiphonon relaxation processes [1-6]. Up to now, many UC fluoride materials (NaYF_4 , NaLuF_4 , LaF_3 , LiYF_4 and NaScF_4) have been successfully prepared by different methods, including hydrothermal method, solvothermal method, high-temperature thermal decomposition of trifluoroacetate precursors and liquid-solid two-phase approaches [7-11]. Among them, NaYF_4 crystal has been considered as one of the most efficient host matrix for UC emission [12-13]. Recently, a new UC host matrix that the NaLuF_4 host matrix with same crystalline plane as NaYF_4 has been reported [14-18]. And Li's group has reported that the $\text{Yb}^{3+}/\text{Er}^{3+}$ and $\text{Yb}^{3+}/\text{Tm}^{3+}$ codoped cubic phase NaLuF_4 nanocrystals (NCs) shown about 10-fold stronger UC emission than that of corresponding hexagonal phase NaYF_4 NCs with same size [19]. As is well known, the hexagonal phase NaYF_4 and NaLuF_4 crystals are evolved from the cubic-phase ones through increasing reaction time or at a high reaction temperature [20-22]. Comparing with the hexagonal phase NaYF_4 and NaLuF_4 crystals, the cubic phase ones can be more easily synthesized through different method. Meanwhile, their UC emission properties can be anticipated to be adjusted by an appropriate method such as changing their crystal phase, morphology and size, and so

on[23]. To date, many researchers have reported that NaLuF₄ is an excellent host matrix for UC luminescence, especially nanoscale NaLuF₄ NCs [24-26].

The strong red UC emission of lanthanide-doped NCs have great potential applications in color display and anticounterfeiting applications, especially for biomedical. However, it is very difficult to obtain a pure single red UC emission from rare earth ions, which because of abundance radiative and nonradiative transition channels of 4f^N electronic states. Consequently, achieving a high-purity single red UC emission has been an increasing focus and formidable challenge. Up to now, there have many reports about obtaining a single-band UC red emission. For example, the intense red emission of Er³⁺ ions in fluoride materials have been successfully obtained by increasing Yb³⁺ ion concentrations, codoping Mn²⁺ or Pb²⁺ ions and attaching noble metal nanoparticles, etc [27-30]. Like Er³⁺ ions, Ho³⁺ ion is also an intriguing active ion for UC emission because of its broad fluorescence spectrum ranging from vacuum ultraviolet to infrared. The enhancement of red UC emission of Ho³⁺ ions in fluoride nanomaterials, however, remain few [31-33]. In this work, we attempted to enhance red UC emission in cubic phase NaLuF₄: Yb³⁺/Ho³⁺ NCs through codoping Ce³⁺ ions. The structure and morphology of NaLuF₄: Yb³⁺/Ho³⁺ NCs were confirmed by x-ray diffraction (XRD) and transmission electron microscope (TEM), respectively. The spectral properties, UC mechanisms and conversion efficiency between Ho³⁺ and Ce³⁺ ions were systematically studied by a confocal microscopy setup under NIR 980 nm and 532 nm excitation. Studies on enhancing the red UC emission in NaLuF₄ NCs will further extend their applications to the three-dimensional color displays,

anticounterfeiting techniques and biological images.

2 Experimental details

2.1 Synthesis of NaLuF₄: Yb³⁺/Ho³⁺/Ce³⁺ NCs

All chemicals used in the current study are analytical grade used without further purification. Ce(NO₃)₃·6H₂O (99.99%), Lu₂O₃ (99.99%), Yb(NO₃)₃·5H₂O (99.99%) and Ho(NO₃)₃·5H₂O (99.99%) are purchased from Sigma-Aldrich Chemicals Co.. Lu(NO₃)₃ was prepared by dissolving the Lu₂O₃ in dilute nitric acid at elevated temperature followed by evaporating the superfluous nitric acid. NaF (Sodium fluoride, 98.0%) and EDTA (ethylenediaminetetraacetic acid, 99.0%) with analytical grade are supplied by the Tianjin chemical reagent factory. The NaLuF₄: Yb³⁺/Ho³⁺/Ce³⁺ NCs were synthesized via a facile hydrothermal method [34]. 5.00 ml NaF (0.5M) and 20.00 ml deionized water were mixed under vigorous stirring. Subsequently, (0.50-x) ml Lu(NO₃)₃ (0.5M), 0.10 ml Yb(NO₃)₃ (0.50M), 0.01 ml Ho(NO₃)₃ (0.50M), x ml (x=0, 0.02, 0.03, 0.04, 0.05, 0.06) Ce(NO₃)₃ (0.50M) and 0.0931g EDTA were slowly added into the solution under vigorous stirring 30 minutes. Then the mixture was slowly transferred into a 40.00 ml Teflon-lined autoclave and heated at 180°C for 8 hours. The samples were collected by centrifuging and washing with deionized water and ethanol 3-4 times, respectively, and dried at 60°C for 12 hours.

2.2 Sample characterization and spectral measurement

The structure and morphology of the samples were characterized by XRD with Cu K α (40 kV, 40 mA) irradiation ($\lambda = 0.15406$ nm) and TEM (JEM2100, 200kV). Fourier transform infrared spectroscopy (FTIR) was measured in the spectral range

400-4000 cm^{-1} with a Bruker EQUINOX55 spectrometer. The optical microscope (OLYMPUS-BX51) is used in the confocal setup. Ti sapphire laser (MBR-110, 700-1000 nm) and YAG: Nd^{3+} (Quanta Ray Lab-170, 10 Hz, 532 nm) pulse laser were employed as excitation sources. The spectrometer (SP2750i, 0.008 nm) with a PIXIS 100 charge coupled device (CCD, ACTON) and a PD471 photomultiplier tube (PMT, ACTON) were used for luminescence collection and detection. All of the spectroscopic measurements were carried out at room temperature.

3 Results and discussion

3.1 Phase identification and morphology characterization.

The typical XRD patterns of NaLuF_4 : 20mol% Yb^{3+} /2mol% Ho^{3+} NCs with codoping different Ce^{3+} concentrations are given in Fig. 1. All the diffraction peaks from NaLuF_4 NCs coincide well with the standard pattern of JCPDS 77-2042, which indexes to the pure cubic phase NaLuF_4 (α - NaLuF_4). In addition, it is noticed that the diffraction peaks shifted slightly to the low angle side after Ce^{3+} ions doping, which indicates the unit cell of α - NaLuF_4 expanded because Lu^{3+} ($r=0.085$ nm) ions are substituted by bigger Ce^{3+} ($r=0.128$ nm) ions in the host lattice [35-36].

The TEM images and EDX spectra of α - NaLuF_4 : Yb^{3+} / Ho^{3+} NCs with codoping different Ce^{3+} ions, as shown in Fig. 2. A series of Ce^{3+} codoped NaLuF_4 : Yb^{3+} / Ho^{3+} NCs are nearly monodisperse nanosphere with an average diameter of about 100 nm. With increasing Ce^{3+} ion concentrations, the morphology and size of α - NaLuF_4 : Yb^{3+} / Ho^{3+} NCs have no obvious effect because of the low dopant concentrations and similar ionic radius. Fig. 2(a1-c1) shows the EDX spectra of

α -NaLuF₄: Yb³⁺/Ho³⁺NCs with doping different Ce³⁺ ions, the elemental components of the samples are Lu, Na, Yb, F, Ho and Ce are clearly presented. It is noted that the peak intensity of the Lu elemental is reduced when the introduction of Ce elemental in α -NaLuF₄: Yb³⁺/Ho³⁺ NCs host lattice, which demonstrates Lu³⁺ ions occupy the lattice sites by the substitution of the Ce³⁺ ions.

3.2 FTIR spectra.

The functional groups attached on the α -NaLuF₄: Yb³⁺/Ho³⁺ NCs can be identified by FTIR spectroscopy, as shown in Fig.3. The strong absorption band around 3400 cm⁻¹ is found, which is attributed to -OH stretching vibration of absorbed EDTA [33]. In addition, the weak bands at 1400 cm⁻¹, 1091 cm⁻¹ and 1640 cm⁻¹ can be assigned to the stretching vibration of -CH₂-, C-O and -COO- group, that originates from the EDTA, respectively [37]. These results prove the existence of EDTA on the surface of the α -NaLuF₄:Yb³⁺/Ho³⁺ NCs, leading to the α -NaLuF₄ NCs can be dispersed into nonpolar solvent or polar solvent. It is found that the intensity of absorption bands of the α -NaLuF₄ NCs has also no evident change with the increase of Ce³⁺ concentrations.

3.3 UC emission of α -NaLuF₄: Yb³⁺/Ho³⁺ NCs with codoping Ce³⁺ ions.

The UC emission of α -NaLuF₄: Yb³⁺/Ho³⁺ NCs with codoping Ce³⁺ ions is carefully investigated by a confocal microscopy system under NIR 980 nm excitation. Figure 4 shows the UC emission spectra, the red-to-green emission (R/G) ratio, the peak area of green and red emission and the Commission Internationale del'Eclairage (CIE) 1931 (x, y) chromaticity coordinates of α -NaLuF₄:Yb³⁺/Ho³⁺ NCs with

codoping different Ce^{3+} ion concentrations, together with their luminescent photographs. The two dominant emission peaks were observed in $\alpha\text{-NaLuF}_4\text{:Yb}^{3+}/\text{Ho}^{3+}$ NCs, 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) of Ho^{3+} ions, respectively [38]. And they also exhibited weak blue and NIR emission, which is associated with the transitions of $^5\text{F}_3 \rightarrow ^5\text{I}_8$ (center at 484 nm) and $^5\text{S}_2/^5\text{F}_4 \rightarrow ^5\text{I}_7$ (center at 750 nm) of Ho^{3+} ions [38]. It is very interesting that the red UC emission intensity increases and the green UC emission intensity decreases with the concentrations of Ce^{3+} increasing from 0mol% to 12mol%. The R/G ratio increases from 1.25 to 12.7. The green/red spectral purity parameter (S_{gr}) of the sample can be estimate according to the literature[39]. S_{gr} values of +1 (−1) correspond to purely green (red) emission. The S_{gr} of the sample is decreased from 0.07 to −0.84 with Ce^{3+} concentrations increasing. This result indicates that the S_{gr} is tuned to red emission, and the corresponding output colors from $\alpha\text{-NaLuF}_4\text{:Yb}^{3+}/\text{Ho}^{3+}$ NCs can be also tuned from yellow region to red region and (in the inset of Fig. 4(a)), which can be further confirmed by the 1931 CIE chromaticity diagram in Fig. 4(d), the corresponding values of (x, y) is listed in the Table 1.

3.4 UC mechanism of $\alpha\text{-NaLuF}_4\text{:Yb}^{3+}/\text{Ho}^{3+}$ NCs with introducing Ce^{3+} ions

To understand the observed phenomenon, the UC emission mechanisms of the green and red are firstly studied. Fig. 5 shows the log–log plot of the UC emission intensities as a function of the infrared excitation pump power for $\alpha\text{-NaLuF}_4\text{:20mol\%Yb}^{3+}/\text{2mol\%Ho}^{3+}$ and $\alpha\text{-NaLuF}_4\text{:20mol\%Yb}^{3+}/\text{2mol\%Ho}^{3+}/\text{12mol\%Ce}^{3+}$ NCs.

The slopes of n for green and red emissions from α -NaLuF₄: 20mol% Yb³⁺/2mol% Ho³⁺ and α -NaLuF₄: 20mol% Yb³⁺/2mol% Ho³⁺/12mol% Ce³⁺ NCs are close to 2, which indicates that the green and red emissions are two photon excitation processes [40]. Noticed that the slopes of n from α -NaLuF₄: 20mol% Yb³⁺/2mol% Ho³⁺/12mol% Ce³⁺ NCs are slightly smaller than that α -NaLuF₄: 20mol% Yb³⁺/2mol% Ho³⁺ 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[41].

To further explore the influence of Ce³⁺ on the emission of Ho³⁺ ions in α -NaLuF₄ NCs, the main processes of radiative transition should be discussed based on the emission spectra. Fig. 6 illustrates a scheme of UC emission processes of Yb³⁺/Ho³⁺/Ce³⁺ system [40, 42]. The main pathway to populate excited states of Ho³⁺ is through the energy transfer (ET) from Yb³⁺ to Ho³⁺ ions, which because Yb³⁺ ions have a larger absorption cross-section for infrared light and longer excited state lifetime than Ho³⁺. Under NIR 980 nm excitation, the excited state ⁵I₆, ⁵F₅ and ⁵S₂/⁵F₄ of Ho³⁺ can be populated by ET processes from neighboring Yb³⁺ ions. When the excited state ⁵S₂/⁵F₄ and ⁵F₅ radiative decay to the ground state ⁵I₈, the green and red UC emissions can be generated. It is found that the red UC emission mainly originates from excited state ⁵F₅, which can be populated through two possible transition processes in Fig. 6. One is the direct population from the nonradiative transition from the excited state ⁵F₄/⁵S₂ of Ho³⁺ ions. The other is from ⁵I₇ to ⁵F₅ state state by through the ET processes from Yb³⁺ to Ho³⁺ ions, and ⁵I₇ state can be populated

through the nonradiative relaxation from the 5I_6 state. Thus, red UC emission intensity of Ho^{3+} ions depends highly on the two nonradiative relaxation processes originate from $^5S_2/^5F_4 \rightarrow ^5F_5$ and $^5I_6 \rightarrow ^5I_7$ transitions. However, according to multiphonon nonradiative relaxation rate $W_{NR} = A \exp^{-BP}$, here, A and B are 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 highest-energy vibrational mode of the host lattice [43].

When the doped ion concentration is low, the interaction of them can be ignored. The multiphonon nonradiative transition rate is mainly decided by the phonon energy of host lattice or surface ligands, such as OH, $-\text{CH}_2$, $-\text{CH}_3$, $\text{C}=\text{O}$ organic groups, etc.[30]. Generally, the multiphonon nonradiative relaxations process dominates over radiative process when the P is less than 5. Since both energy gaps of $^5S_2/^5F_4 \rightarrow ^5F_5$ and $^5I_6 \rightarrow ^5I_7$ are about 3000 cm^{-1} , which is approximately eight times higher than that the maximum phonon energy of flouride hosts is less than 360 cm^{-1} [44-45]. Thus, the UC emission from Yb^{3+} and Ho^{3+} ions codoped $\alpha\text{-NaLuF}_4$ should exhibit intense green emission and accompany with weak red emission [46]. However, the output color of $\alpha\text{-NaLuF}_4$: 20mol% Yb^{3+} /2mol% Ho^{3+} NCs is yellow, not green in Fig. 4, which may be ascribed to the effectiveness of the multiphonon relaxation process due to the existence of EDTA based on the results of FTIR spectroscopy in Fig. 3 [30]. The similar phenomena were also observed in Y_2O_3 : Yb^{3+} / Er^{3+} and NaYF_4 : Yb^{3+} / Er^{3+} NCs [46-47]. Nevertheless, the more high R/G ratio is observed in $\alpha\text{-NaLuF}_4$: 20mol% Yb^{3+} /2mol% Ho^{3+} NCs when Ce^{3+} ions are introduced to the system, as shown in Figure 4(b). When the Ce^{3+} ion concentration is increased 12mol%, the R/G ratio is

enhanced 10-fold. Since the energy gap between the excited state $^5F_{7/2}$ and ground state $^2F_{5/2}$ is about 3000 cm^{-1} of Ce^{3+} ion is similar to the energy gaps of $^5S_2/^5F_4 \rightarrow ^5F_5$ and $^5I_6 \rightarrow ^5I_7$ of Ho^{3+} ions [46]. The two inefficient nonradiative processes of $^5S_2/^5F_4 \rightarrow ^5F_5$ and $^5I_6 \rightarrow ^5I_7$ transitions of Ho^{3+} ions can be replaced in order by cross relaxation (CR) processes of $^5S_2(^5F_4) (\text{Ho}^{3+}) + ^2F_{5/2} (\text{Ce}^{3+}) \rightarrow ^5F_5 (\text{Ho}^{3+}) + ^2F_{7/2} (\text{Ce}^{3+})$ and $^5I_6 (\text{Ho}^{3+}) + ^2F_{5/2} (\text{Ce}^{3+}) \rightarrow ^5I_7 (\text{Ho}^{3+}) + ^2F_{7/2} (\text{Ce}^{3+})$ between Ho^{3+} and Ce^{3+} ions, which can efficiently enhance red emission and suppress green emission.

Fig. 7(a) shows NIR (1175 nm) emission of $^5I_6 \rightarrow ^5I_8$ transition of Ho^{3+} ions in $\alpha\text{-NaLuF}_4\text{: Yb}^{3+}/\text{Ho}^{3+}$ NCs with codoping different Ce^{3+} ion concentrations under 980 nm excitation. The relative intensity of NIR emission decreases when the Ce^{3+} ion concentrations increase from 0mol% to 12.0mol%, as shown in Fig.7(b). Well is it known that the fluorescence emission intensity mainly relies on the competition between radiative relaxation and nonradiative relaxation. Consequently, the NIR emission intensity decreases with the increase of Ce^{3+} concentrations indicates that 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+} ions.

The occurrence of CR2 process $^5S_2/^5F_4 (\text{Ho}^{3+}) + ^2F_{5/2} (\text{Ce}^{3+}) \rightarrow ^5F_5 (\text{Ho}^{3+}) + ^2F_{7/2} (\text{Ce}^{3+})$ between Ho^{3+} and Ce^{3+} can be further proved based on the intensity of downconversion (DC) emission of Ho^{3+} in $\alpha\text{-NaLuF}_4\text{: Yb}^{3+}/\text{Ho}^{3+}$ NCs under 532 nm pulsed laser excitation. The $^5S_2/^5F_4$ excited states can be directly populated by 532 nm pulsed laser, and generates green emission by radiative decay from $^5S_2/^5F_4 \rightarrow ^5I_8$ transition. The red emission originates from 5F_5 state. It is noticed that the green

emission intensity reduces and red emission increases with, and the corresponding R/G ratio is enhanced from 0.33 to 0.80 in Figure 8. According to the above discussion from Figure 5, the nonradiative process of $^5S_2/^5F_4 \rightarrow ^5F_5$ transition is inefficient. Therefore, the R/G ratio of Ho^{3+} in $\alpha-NaLuF_4: Yb^{3+}/Ho^{3+}/Ce^{3+}$ NCs is increased mainly with the increase of Ce^{3+} concentrations, which can be attributed to the occurrence of CR2 process between Ho^{3+} and Ce^{3+} ions.

3.5 The conversion efficiency of CR1 and CR2 processes

The conversion efficiency of CR processes between Ho^{3+} and Ce^{3+} ions can be calculated based on the steady-state rate equations and decay lifetime. According to the proposed energy transfer UC process of $Yb^{3+}-Ho^{3+}-Ce^{3+}$ triply doped system as shown in Fig. 5. In the case of continuous wave laser excitation, the rate equations of each energy state are formulated as follows [32,49-50]:

$$r_1 n_2 n_{Ce0} - R_1 n_1 - w_1 n_{Yb1} n_1 = 0 \quad (1a)$$

$$w_0 n_{Yb1} n_0 - r_1 n_2 n_{Ce0} - R_2 n_2 - w_2 n_{Yb1} n_1 = 0 \quad (1b)$$

$$w_1 n_{Yb1} n_1 + r_2 n_4 n_{Ce0} - R_3 n_3 = 0 \quad (1c)$$

$$w_2 n_{Yb1} n_2 - R_4 n_4 - r_2 n_4 n_{Ce0} = 0 \quad (1d)$$

where, n_0 , n_1 , n_2 , n_3 and n_4 refer to the population densities of the 5I_8 , 5I_7 , 5I_6 , 5F_5 and $^5S_2(^5F_4)$ states of the Ho^{3+} ions, respectively n_{Yb0} and n_{Yb1} are the population densities of the $^2F_{7/2}$ and $^2F_{5/2}$ levels of the Yb^{3+} ions. n_{Ce0} represents the population densities of the $^2F_{5/2}$ levels of the Ce^{3+} ions. w_0 , w_1 and w_2 are ET rates from the Yb^{3+} ions to Ho^{3+} ions, n_{Yb1} to n_{Yb0} and n_0 to n_2 , n_{Yb1} to n_{Yb0} and n_1 to n_3 , n_{Yb1} to n_{Yb0} and n_2 to n_4 , respectively R_1 , R_2 , R_3 and R_4 are the intrinsic decay rates rates of the $^5I_7 \rightarrow ^5I_8$,

$^5I_6 \rightarrow ^5I_8$, $^5F_5 \rightarrow ^5I_8$ and $^5S_2(^5F_4) \rightarrow ^5I_8$ of the Ho^{3+} ions, respectively r_1 and r_2 are the rate for Ho^{3+} ions to Ce^{3+} CR process $^5I_6 (\text{Ho}^{3+}) + ^2F_{5/2} (\text{Ce}^{3+}) \rightarrow ^5I_7 (\text{Ho}^{3+}) + ^2F_{7/2} (\text{Ce}^{3+})$ and $^5S_2/^5F_4 (\text{Ho}^{3+}) + ^2F_{5/2} (\text{Ce}^{3+}) \rightarrow ^5F_5 (\text{Ho}^{3+}) + ^2F_{7/2} (\text{Ce}^{3+})$, respectively. Generally, the intrinsic decay rates at the intermediate states are much larger than the UC rates [41]. The emission intensity of NIR ($^5I_6 \rightarrow ^5I_8$) of Ho^{3+} ions can be estimated according to equation 1, we can get:

$$I_{\text{NIR}} = n_2 h \nu_{\text{NIR}} R_2 = \frac{R_2}{R_2 + r_1 n_{\text{Ce}0}} h \nu_{\text{NIR}} w_1 n_0 n_{\text{Yb}1} \quad (4)$$

Based on the measured fluorescence emission intensity of NIR in Fig.7 and equation 4, we have

$$\frac{I_{\text{NIR}}(0\% \text{Ce})}{I_{\text{NIR}}(12.0\% \text{Ce})} = \frac{R_2 + r_1 n_{\text{Ce}0}}{R_2} = 1 + \frac{r_1 n_{\text{Ce}0}}{R_2} = 5.74 \quad (5)$$

The conversion efficiency of the CR1 process [32]:

$$\eta_1 = \frac{\beta + r_1 n_{\text{Ce}0}}{R_2 + r_1 n_{\text{Ce}0}} \approx \frac{r_1 n_{\text{Ce}0}}{R_2 + r_1 n_{\text{Ce}0}} = 82.65\% \quad (6)$$

The conversion efficiency of CR2 process can be calculated with the following equation[51]:

$$\eta_2 = 1 - \frac{\tau(12\% \text{Ce})}{\tau'(0\% \text{Ce})} = 39.72\% \quad (7)$$

The evolution of lifetime decays of the green emission at 541 nm of Ho^{3+} in $\alpha\text{-NaLuF}_4$: 20mol% Yb^{3+} /2mol% Ho^{3+} NCs and $\alpha\text{-NaLuF}_4$: 20mol% Yb^{3+} /2mol% Ho^{3+} /12mol% Ce^{3+} NCs under 532 nm pulsed laser as shown in Fig. 9. The η_1 is much higher than the η_2 , which indicates that the CR2 plays an assistant role for the CR1 process in converting the green UC emission into red UC emission.

4 Conclusions

The pure α -NaLuF₄:Yb³⁺/Ho³⁺/Ce³⁺ NCs have been successfully synthesized by a facile hydrothermal method. The intense red UC emission has been observed in α -NaLuF₄: Yb³⁺/Ho³⁺/Ce³⁺ NCs. The R/G ratio is effectively boosted 10-fold with the Ce³⁺ ion doped concentrations are increased to 12mol%, which is mainly due to the two efficient CR processes of $^5S_2/^5F_4$ (Ho³⁺) + $^2F_{5/2}$ (Ce³⁺) $\rightarrow$ 5F_5 (Ho³⁺) + $^2F_{7/2}$ (Ce³⁺) and 5I_6 (Ho³⁺) + $^2F_{5/2}$ (Ce³⁺) $\rightarrow$ 5I_7 (Ho³⁺) + $^2F_{7/2}$ (Ce³⁺) between Ho³⁺ and Ce³⁺ promoted the red emission and quenched the green emission, respectively. The strong red UC emission depends highly on CR1 process. The high-purity single red UC emission from α -NaLuF₄:Yb³⁺/Ho³⁺/Ce³⁺ NCs could be useful for color display and anticounterfeiting application.

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Graphical Abstract

The upconversion emission of Ho^{3+} was tuned from green to red because of two efficient cross relaxation between Ho^{3+} with Ce^{3+} .

Figure captions

Fig. 1 XRD patterns of α -NaLuF₄: 20%Yb³⁺/2%Ho³⁺/xCe³⁺ NCs (x=0%, 4%, 6%, 8% and 12%).

Fig. 2 TEM images and EDX spectra of α -NaLuF₄: 20%Yb³⁺/2%Ho³⁺ NCs with Ce³⁺ ions of 0%, 6% and 12%.

Fig. 3 FTIR spectra of α -NaLuF₄: 20%Yb³⁺/2%Ho³⁺ NCs with doping different Ce³⁺ ions.

Fig. 4 (a) UC emission spectra, (b) R/G ratio, (c) the peak area of the green and red emission, and (d) CIE diagram of α -NaLuF₄: Yb³⁺/Ho³⁺ NCs for different Ce³⁺ ion concentrations under 980 nm excitation. The inset is corresponding luminescence photographs.

Fig. 5 Pump power dependence of α -NaLuF₄: 20%Yb³⁺/2%Ho³⁺/xCe³⁺ NCs (x=0% (a) and 12% (b)).

Fig. 6 Energy level diagrams of Ho³⁺, Yb³⁺ and Ce³⁺ ions as well as proposed UC mechanisms.

Fig. 7 (a) The NIR spectra and (b) the relative intensity of ⁵I₆→⁵I₈ transition of Ho³⁺ in α -NaLuF₄: 20%Yb³⁺/2%Ho³⁺ NCs with Ce³⁺ ion concentrations increasing from 0% to 12% under 980 nm excitation.

Fig. 8 (a) The DC emission spectra, (b) the peak area of the green and red emission and (c) R/G ratio of Ho³⁺ ions of α -NaLuF₄: 20%Yb³⁺/2%Ho³⁺ NCs with codoping different Ce³⁺ ions under pulse laser 532 nm excitation.

Fig. 9 DC luminescence decays of the ⁵S₂/⁵F₄ →⁵I₈ transition at 541 nm of Ho³⁺ for

α -NaLuF₄: 20% Yb³⁺/2% Ho³⁺/xCe³⁺ NCs (x=0% and 12%). The luminescence decay curves are fitted by using a single exponential function.

Fig. 1

Fig. 2

Fig. 3

Fig. 4

Fig. 5

Fig. 6

Fig. 7

Fig. 8

Fig. 9

TABLE

Table 1 The calculated CIE chromaticity coordinates (x , y) of α -NaLuY₄: Yb³⁺/Ho³⁺ NCs with different Ce³⁺ ions.

Point	Samples	CIE chromaticity coordinates	
		x	y
a	α -NaLuF ₄ : 20% Yb ³⁺ /2% Ho ³⁺	0.3712	0.5542
b	α -NaLuF ₄ : 20% Yb ³⁺ /2% Ho ³⁺ /4% Ce ³⁺	0.4126	0.4813
c	α -NaLuF ₄ : 20% Yb ³⁺ /2% Ho ³⁺ /6% Ce ³⁺	0.4713	0.4327
d	α -NaLuF ₄ : 20% Yb ³⁺ /2% Ho ³⁺ /8% Ce ³⁺	0.4927	0.3826
d	α -NaLuF ₄ : 20% Yb ³⁺ /2% Ho ³⁺ /10% Ce ³⁺	0.5421	0.3417
e	α -NaLuF ₄ : 20% Yb ³⁺ /2% Ho ³⁺ /12% Ce ³⁺	0.5814	0.2876