Near-Infrared Quantum Cutting in $\text{Ho}^{3+}/\text{Yb}^{3+}$ Co-doped $\text{BaZr}_{0.8}\text{Y}_{0.2}\text{O}_{3-\delta}$

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Abstract

A novel $\text{Ho}^{3+} \rightarrow \text{Yb}^{3+} \rightarrow \text{Ho}^{3+}$ multi-step energy transfer caused quantum cutting under 455 nm excitation is observed in $\text{Ho}^{3+}/\text{Yb}^{3+}$ co-doped $\text{BaZr}_{0.8}\text{Y}_{0.2}\text{O}_{3-\delta}$ phosphor. During the quantum cutting process, Yb^{3+} ions efficiently increase the particle population of $^5\text{I}_6$ level of Ho^{3+} , resulting in 10 and 8 times of enhancement of Ho^{3+} emission at 1216 nm ($^5\text{I}_6 \rightarrow ^5\text{I}_8$) and 1926 nm ($^5\text{I}_7 \rightarrow ^5\text{I}_8$), respectively. It is interesting that the $^2\text{F}_{5/2} \rightarrow ^2\text{F}_{7/2}$ emission of Yb^{3+} ions themselves is very weak although the quantum cutting is performed by the $\text{Ho}^{3+}/\text{Yb}^{3+}$ ion-pairs. The result indicates that the $\text{Yb}^{3+} \rightarrow \text{Ho}^{3+}$ back energy transfer in the $\text{BaZr}_{0.8}\text{Y}_{0.2}\text{O}_{3-\delta}$ phosphor is quite efficient and helpful for the enhancement of Ho^{3+} emission in near infrared region. A new valid method based on luminescence intensity ratio is developed to estimate the quantum cutting efficiency. It is found that the energy transfer from Ho^{3+} to Yb^{3+} is 52.8% in the phosphor with optimum $\text{Ho}^{3+}/\text{Yb}^{3+}$ doping concentration and 90% of near infrared emission of Ho^{3+} is performed by the multi-step energy transfer induced quantum cutting.

1. Introduction

Luminescent materials with quantum efficiency (QE) higher than unity have attracted great interests for their potential application in the fields of plasma displays, mercury-free fluorescent lamps, solar cells and so on[1]. In recent decades, rare-earth-doped materials with near-infrared down-conversion (DC) quantum cutting (QC) luminescence have attracted great attention for their potential applications in photovoltaic solar cells or photo-detectors based on crystalline Si[2-7]. Many $\text{Ln}^{3+}/\text{Yb}^{3+}$ couples such as $\text{Tm}^{3+}/\text{Yb}^{3+}$ [8], $\text{Pr}^{3+}/\text{Yb}^{3+}$ [6], $\text{Tb}^{3+}/\text{Yb}^{3+}$ [2], $\text{Er}^{3+}/\text{Yb}^{3+}$ [4] and $\text{Nd}^{3+}/\text{Yb}^{3+}$ [3] that can convert near ultraviolet or visible photons into near-infrared photons have been witnessed.

According to the properties of the energy-transfer process, the DC QC performed by $\text{Ln}^{3+}/\text{Yb}^{3+}$ pairs can be divided into two types—one is first-order DC and the other is second-order DC[9]. First-order DC is a cross relaxation process occurring between couples of matched energy levels, while second-order DC is a process during which a sensitized ion at high level transfers its energy to two other luminous ions at a lower energy level. It is believed that first-order QC may have a higher probability than the second-order one. However, efficient DC using Yb^{3+} via resonant energy transfer requires donor ions with an energy level at about $20\,000\text{ cm}^{-1}$ and an intermediate energy level at approximately $10\,000\text{ cm}^{-1}$. Consequently efficient first-order DC can be expected only for the couples $\text{Pr}^{3+}/\text{Yb}^{3+}$, $\text{Nd}^{3+}/\text{Yb}^{3+}$, $\text{Er}^{3+}/\text{Yb}^{3+}$ and $\text{Ho}^{3+}/\text{Yb}^{3+}$ [9]. Among these $\text{Ln}^{3+}/\text{Yb}^{3+}$ couples, $\text{Ho}^{3+}/\text{Yb}^{3+}$ couple is a good choice in NIR QC investigation because of the favorable metastable energy levels of Ho^{3+} ion and

considerable energy match between Yb^{3+} and Ho^{3+} . Moreover, $\text{Ho}^{3+}/\text{Yb}^{3+}$ couple is capable to convert both Near UV and visible light into near infrared emission due the level structure of Ho^{3+} . Recently NIR QC in $\text{Ho}^{3+}/\text{Yb}^{3+}$ -co-doped materials such as $\text{Y}_2\text{O}_3:\text{Yb}^{3+}/\text{Ho}^{3+}$ [10], $\beta\text{-NaYF}_4:\text{Ho}^{3+}/\text{Yb}^{3+}$ [11] has been reported. Nevertheless, the QC properties of $\text{Ho}^{3+}/\text{Yb}^{3+}$ couple in different hosts are still worth exploring.

Over the past decade, rare earth doped ABO_3 -like oxide with perovskite structure have been reported possessing very interesting luminescent properties. The ABO_3 -like oxides have in the A-site a divalent alkaline earth element, such as Ba, Sr and Ca, and in the B-site a tetravalent element (Ce, Zr, Ti)[12, 13]. The perovskite-type oxides phosphors are very stable and can steadily work in various environments[14]. Moreover, perovskite-type oxides phosphors have been found to be potential candidate in field emission display (FED) and plasma display panel (PDP) devices because they are sufficiently conductive to release electric charges stored on the phosphor particle surfaces[15]. Thus a great deal of perovskite-type oxides phosphors activated by rare earth ions, including Ce^{3+} , Sm^{3+} , Tm^{3+} , Pr^{3+} , Eu^{3+} , Tb^{3+} and so forth[16-21] have been prepared and their luminescent properties were investigated. On the other hand, the studies on up-conversion of $\text{Yb}^{3+}/\text{Tm}^{3+}$ [22] and $\text{Yb}^{3+}/\text{Er}^{3+}$ [23] co-doped perovskite-type oxide phosphors have also been reported. However, there are few reports on DC emission of rare earth ions in perovskite-type oxides.

BaZrO_3 doped with rare earth ions, is one of widely investigated perovskite-type phosphors [22, 23]. In ordinary BaZrO_3 host, doped trivalent rare earth ions tend to substitute octahedral Zr^{4+} sites[24, 25]. The electric dipole f-f transitions of trivalent

rare earth ions are strictly forbidden in a regular octahedral field according to the selection rule. Fortunately, the ZrO_6 -octahedron is usually distorted in BaZrO_3 matrix. Meanwhile, the substitution of Zr^{4+} sites by trivalent rare earth ions will result in O^{2-} vacancies due to the charge imbalance between Zr^{4+} and Ln^{3+} ions. The two factors alter the local symmetry around the doped trivalent rare earth ions and make the f-f transition of trivalent rare earth possible. It is reported that 1/5 of Zr^{4+} ions can be replaced by Y^{3+} in BaZrO_3 , forming a $\text{BaZr}_{0.8}\text{Y}_{0.2}\text{O}_{3-\delta}$ oxide without changing the basic structure [26-29]. In the $\text{BaZr}_{0.8}\text{Y}_{0.2}\text{O}_{3-\delta}$ oxide, the heavily doped Y^{3+} ions and a large amount of O^{2-} vacancies caused by Y^{3+} doping might effectively adjust the local symmetry around the rare earth ions. Thus increased the f-f transition of the doped trivalent rare earth is expected.

Herein, in the present work, we prepared $\text{Ho}^{3+}/\text{Yb}^{3+}$ co-doped $\text{BaZr}_{0.8}\text{Y}_{0.2}\text{O}_{3-\delta}$ oxides with perovskite structure have been synthesized by co-precipitation method. The crystalline structures, NIR QC luminescence properties of phosphors with different concentrations of Ho^{3+} and Yb^{3+} ions are studied and the QC mechanism in $\text{Ho}^{3+}/\text{Yb}^{3+}$ co-doped $\text{BaZr}_{0.8}\text{Y}_{0.2}\text{O}_{3-\delta}$ phosphors is discussed in detail.

2. Experimental

Co-precipitation technique is a good method for preparation of luminescent material with relatively high melting point, which can make the raw material refining and homogeneous mixing, lower the calcinations temperature and reduce the calcinations time. Therefore, in our experiment, the $\text{BaZr}_{0.8-x}\text{Y}_{0.2-y}\text{O}_{3-\delta} : x\text{Ho}^{3+}, y\text{Yb}^{3+}$ ($x=0.01, 0.02, 0.05, 0.1, 0.15, 0.2$; $y=0, 0.01, 0.02, 0.05, 0.08, 0.12, 0.15$,

0.18, 0.2) samples were prepared by the co-precipitation synthesis procedure. Zirconium oxychloride octahydrate ($\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$), barium chloride dehydrate ($\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$), Yttrium oxide (Y_2O_3), Ytterbium oxide (Yb_2O_3), Holmium oxide (Ho_2O_3), nitric acid (HNO_3) and ammonium hydroxide ($\text{NH}_3 \cdot \text{H}_2\text{O}$) were used as the starting materials. All the reagents were of the analytical purity. A procedure for the sample synthesis of $\text{BaZr}_{0.8}\text{Y}_{0.2}\text{O}_{3-\delta}$: Yb^{3+} - Ho^{3+} is typically described as follows: firstly Y_2O_3 , Yb_2O_3 and Ho_2O_3 were dissolved in dilute nitric acid under condition of stirring and heating, respectively. After the Y_2O_3 , Yb_2O_3 and Ho_2O_3 were completely dissolved, the excess nitrite acid was removed at high temperature. Then a certain amount of de-ionized water was added to obtain $\text{Y}(\text{NO}_3)_3$, $\text{Yb}(\text{NO}_3)_3$ and $\text{Ho}(\text{NO}_3)_3$ solution with concentration of 1mol/L. $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ and $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ were also dissolved in de-ionized water to obtain the solution with concentration of 1mol/L and 0.1mol/L, respectively. Subsequently, these solutions were mixed with proper ratio according to the designed target product, and stirred for 0.5 h to obtain a new homogeneous solution. Then the white precipitate was formed by slowly dropped $\text{NH}_3 \cdot \text{H}_2\text{O}$ with magnetic stirring. The precipitate was filtrated and washed four times with de-ionized water, and then twice with ethyl alcohol, and followed by drying at 120 °C for 24 h. In the end, the precipitate was pre-sintering at 550°C for 3 h to obtain the white powder. the powder was grinded and annealed at 1100°C for 3 h in air to obtain the white phosphor sample.

The structure of the samples was identified by X-ray diffraction (XRD) on a Bruker D8 advance equipment using Cu tube with $\text{K}\alpha$ radiation of 0.15406 nm in the

2 θ range of 20° to 80°. The emission spectra were obtained by a monochromator (Zolix Instrument, Omni- λ 320i) coupled with photomultiplier (PMTH-S1-CR131) and NIR sensitive detector (DInGaAs 2600-TE). Diode lasers at 455 nm and 980 nm were used as excitation sources in the measurement. The luminescence decay curves were measured by a FLS920 (Edinburgh) spectrometer. All the measurements were performed at room temperature.

3. Results and discussion

Fig. 1 shows the powder X-ray diffraction patterns of the $\text{BaZr}_{0.8-x}\text{Y}_{0.2-y}\text{O}_{3-\delta}:\text{xHo}^{3+}, \text{yYb}^{3+}$ ($x=0.05, 0.1, 0.2; y=0, 0.05, 0.12, 0.15, 0.2$) powders. The diffraction peaks of the XRD pattern of $\text{BaZr}_{0.8-x}\text{Y}_{0.2-y}\text{O}_{3-\delta}:\text{xHo}^{3+}, \text{yYb}^{3+}$ are consistent with that of standard powder diffraction of $\text{BaZr}_{0.8}\text{Y}_{0.2}\text{O}_{3-\delta}$ [30, 31], indicating that all of the $\text{BaZr}_{0.8-x}\text{Y}_{0.2-y}\text{O}_{3-\delta}:\text{xHo}^{3+}, \text{yYb}^{3+}$ compounds were successfully synthesized with the co-precipitation method. The prepared $\text{BaZr}_{0.8-x}\text{Y}_{0.2-y}\text{O}_{3-\delta}:\text{xHo}^{3+}, \text{yYb}^{3+}$ compounds also have cubic perovskite-structure belonging to the Pm-3m space group. It is believed that in $\text{BaZr}_{0.8}\text{Y}_{0.2}\text{O}_{3-\delta}$ host Y^{3+} ($\text{Yb}^{3+}, \text{Ho}^{3+}$) ions usually occupied Zr^{4+} sites [21, 32].

Fig. 1 Powder X-ray diffraction patterns of the $\text{BaZr}_{0.8-x}\text{Y}_{0.2-y}\text{O}_{3-\delta} : x\text{Ho}^{3+}, y\text{Yb}^{3+}$ ($x=0.05, 0.1, 0.2$; $y=0, 0.05, 0.12, 0.15, 0.2$) powders.

The luminescence spectra in NIR region of $\text{BaZr}_{0.8}\text{Y}_{0.2}\text{O}_{3-\delta}$ doped with various concentrations of Ho^{3+} ions (fixed Yb^{3+} concentration at 12%) on the 455 nm excitation are shown in **Fig. 2**. NIR PL peaked at 1216 nm ($\text{Ho}^{3+}: ^5\text{I}_6 \rightarrow ^5\text{I}_8$) and 1926 nm ($\text{Ho}^{3+}: ^5\text{I}_7 \rightarrow ^5\text{I}_8$) were observed for all the samples. The relationship of 1216 nm and 1926 nm intensities tendency with Ho^{3+} ions concentrations are also given in the inset of **Fig. 2**. It is found that the integrated intensities of the NIR emission bands centred at 1216 nm and 1926 nm increase firstly and then decrease with the increasing concentration of Ho^{3+} , respectively. Both 1216 nm and 1926 nm emissions reach their

maximum intensities when the Ho^{3+} concentration is 10%. With Ho^{3+} concentration increasing, more Ho^{3+} ions in the phosphor can absorb the excitation light and the energy transfer (ET) from Ho^{3+} to Yb^{3+} ion and back energy transfer (BET) from Yb^{3+} to Ho^{3+} ions also become more efficient due to the shortened distance between the Yb^{3+} and Ho^{3+} ions. As a result, the near infrared emission intensities increase as Ho^{3+} concentration increases. However, the 1216 nm and 1926 nm emission intensities tend to decrease with further increasing the Ho^{3+} ion concentration owing to the concentration quenching effect.

Fig. 2 NIR Photoluminescence spectra of $\text{BaZr}_{0.8}\text{Y}_{0.2}\text{O}_{3-\delta}$ phosphors with diverse Ho^{3+} concentrations when Yb^{3+} concentration fixed at 12% under excitation of 455 nm. The inset shows the 1216 nm and 1926 nm emission intensities tendency when changing the Ho^{3+} concentration

After the optimum doping concentration Ho^{3+} is confirmed, the Yb^{3+}

concentration dependent near infrared emission is further investigated. **Fig. 3** shows visible-NIR emission luminescence spectra of $\text{BaZr}_{0.8}\text{Y}_{0.2}\text{O}_{3-\delta}$ doped with various concentrations of Yb^{3+} ions (fixed Ho^{3+} concentration at 10%) under 455nm excitation. In the inset of **Fig. 3 (a)**, the integrated intensity of the NIR emission band centred at 1216 nm and 1926 nm also become stronger with increasing Yb^{3+} concentration when the concentration of Ho^{3+} is fixed at 10%, and reach their maximum at 12%. The 1216 nm and 1926 nm intensities become weaker when the Yb^{3+} concentration increases beyond 12%, because of the concentration quenching. Therefore, the $\text{BaZr}_{0.7}\text{Y}_{0.08}\text{O}_{3-\delta} : 0.1\text{Ho}^{3+}, 0.12\text{Yb}^{3+}$ sample is believed to possess the optimum doping concentration to give the strongest near infrared emission in our experiment. **Fig. 3(b)** shows the amplified spectra in the range 900 nm – 1060 nm under 455 nm excitation, with various concentrations of Yb^{3+} ions (fixed Ho^{3+} concentration at 10%). It is found that that the Yb^{3+} concentration dependent transition intensity of $^2\text{F}_{5/2} \rightarrow ^2\text{F}_{7/2}$ of Yb^{3+} is similar to that of $^5\text{I}_6 \rightarrow ^5\text{I}_8$ (1216 nm) and $^5\text{I}_7 \rightarrow ^5\text{I}_8$ (1926 nm) of Ho^{3+} . However, the $^2\text{F}_{5/2} \rightarrow ^2\text{F}_{7/2}$ emission intensity of Yb^{3+} is about 100 and 25 times weaker than the $^5\text{I}_6 \rightarrow ^5\text{I}_8$ and $^5\text{I}_7 \rightarrow ^5\text{I}_8$ emission intensity of Ho^{3+} , respectively.

To understand the mechanism of NIR emissions, the luminescence spectra in visible region have also been measured, given in **Fig. 3 (c)**. Green emission at 556 nm and weak red emissions at 660 nm and 760 nm can be observed under 455 nm excitation, which are ascribed the $^5\text{F}_4(^5\text{S}_2) \rightarrow ^5\text{I}_8$, $^5\text{F}_5 \rightarrow ^5\text{I}_8$, and $^5\text{F}_4(^5\text{S}_2) \rightarrow ^5\text{I}_7$ transitions of Ho^{3+} , respectively. Unlike the near infrared emission, the visible emissions always decrease gradually with Yb^{3+} concentration increasing.

Fig. 3 (a) Emission spectra of the samples in the NIR range under excitation of 455 nm. The inset shows the 1216 nm and 1926 nm emissions intensity tendency when changing the Yb³⁺ concentration. (b) Amplified Emission spectra in the range 900 nm – 1060 nm, (c) Emission spectra of the samples in the visible range under excitation of 455 nm.

The increased near infrared emission and decreased visible emission with the introduction of Yb³⁺ clearly indicates that an energy transfer QC from Ho³⁺ to Yb³⁺. The most possible energy transfer is Ho³⁺ (⁵F₄, ⁵S₂) + Yb³⁺ (²F_{7/2}) → Ho³⁺ (⁵I₆) + Yb³⁺ (²F_{5/2}), considering the energy level matching between the two ions[10, 11]. Obviously, a back energy transfer Ho³⁺ (⁵I₈) + Yb³⁺ (²F_{5/2}) → Ho³⁺ (⁵I₆) + Yb³⁺ (²F_{7/2}) is easily to take place[10] when the Yb³⁺ ions are excited by the energy transfer process.

To illustrate the back energy transfer process from Yb³⁺ to Ho³⁺, the NIR spectra in region of 1000-1300 nm for BaZr_{0.7}Y_{0.2-x}O_{3-δ}: xYb³⁺, 0.1Ho³⁺ (fixed

Ho³⁺ concentration at 10%) samples is measured under 980 nm excitation, shown in **Fig. 4**. The emission band corresponding to the ⁵I₆ → ⁵I₈ transition of Ho³⁺ ions is also observed and its intensity increases with Yb³⁺ concentration increasing, indicating the energy transfer Ho³⁺ (⁵I₈) + Yb³⁺ (²F_{5/2}) → Ho³⁺ (⁵I₆) + Yb³⁺ (²F_{7/2}) can occur as long as Yb³⁺ ions are excited to their ²F_{5/2} state. It is also noted that the 1216 nm NIR luminescence weakens when the Yb³⁺ concentration increases beyond 12%, which means the concentration quenching is also inevitable at high Yb³⁺ concentration.

Fig. 4 NIR PL spectra under excitation of 980 nm (Yb³⁺: ⁵F_{7/2} → ⁵F_{5/2}) of BaZr_{0.7}Y_{0.2-x}O_{3-δ}:

10%Ho³⁺, x%Yb³⁺ (1 ≤ x ≤ 18)

According to above discussion, the QC down-conversion mechanism between Ho³⁺ and Yb³⁺ ions can be described in **Fig. 5**. On the 455 nm excitation, Ho³⁺ ion

absorbs a photon and jumps from the ground state 5I_8 to the excited state 5G_6 and then relaxes to the 5F_4 state by non-radiative process. The followed two energy transfer pathways between Ho^{3+} and Yb^{3+} ions perform the quantum cutting. The first one is energy transfer: $Ho^{3+} (^5F_4, ^5S_2) + Yb^{3+} (^2F_{7/2}) \rightarrow Ho^{3+} (^5I_6) + Yb^{3+} (^2F_{5/2})$ and the second one is back energy transfer: $Ho^{3+} (^5I_8) + Yb^{3+} (^2F_{5/2}) \rightarrow Ho^{3+} (^5I_6) + Yb^{3+} (^2F_{7/2})$. Obviously, both the energy transfer and back energy transfer processes can increase the population of 5I_6 level, effectively enhancing the near infrared emission intensity of Ho^{3+} . It is note that the 900 - 1060 nm emission of Yb^{3+} is very weak whether at low or high Yb^{3+} and Ho^{3+} doping concentrations, which is quite different from other Yb^{3+}/Ho^{3+} co-doped down-conversion phosphors reported [1, 10, 11, 33, 34]. This indicates that in $BaZr_{0.8}Y_{0.2}O_{3-\delta}$ host the rate of back energy transfer process from Yb^{3+} to Ho^{3+} is much larger than the radiative emission rate of Yb^{3+} itself, making the down-conversion more efficient.

Fig. 5 Schematic diagram of the energy levels of Ho^{3+} and Yb^{3+} and possible energy transfer routes between Ho^{3+} and Yb^{3+} upon the 455 nm excitation

Based on the intensity ratios of the 556 nm emission of the Ho^{3+} singly doped and $\text{Ho}^{3+}/\text{Yb}^{3+}$ co-doped samples, we develop a new method to estimate the energy transfer and down-conversion efficiency. Under 455 nm excitation, the measured intensity at 556 nm caused by the Ho^{3+} ($^5\text{S}_2 \rightarrow ^5\text{I}_6$) transition at different Yb^{3+} concentration is expressed as

$$I_{x\% \text{Yb}} = kh\nu\omega(1 - \eta_{\text{ET}})N. \quad (1)$$

Where h is Planck constant, k is a constant determined by the responsibility of the detection system, ν is the frequency of the 556 nm emission of Ho^{3+} , ω is the radiative rate of the $^5\text{F}_4(^5\text{S}_2)$ level of Ho^{3+} , N is the number of the Ho^{3+} ions at $^5\text{F}_4(^5\text{S}_2)$ state excited by 455 nm excitation.

The 556 nm emission intensity ratio R between $\text{Ho}^{3+}/\text{Yb}^{3+}$ co-doped and Ho^{3+} singly doped sample is then written as

$$R = I_{x\%Yb}/I_{0\%Yb} = kh\nu(1 - \eta_{ET})\omega N/kh\nu\omega N. \quad (2)$$

When the test condition is identical and the 455 nm excitation power is fixed for all the samples during the measurement, energy transfer efficiency η_{ET} can be expressed as

$$\eta_{ET} = 1 - I_{x\%Yb}/I_{0\%Yb}. \quad (3)$$

Where $I_{0\%Yb}$ and $I_{x\%Yb}$ are the green (556 nm) luminescence intensity of the samples in the absence and presence of Yb^{3+} ($x=1, 5, 12, 15, 18$). With Eq. (3), it is easy to calculate the energy transfer efficiency η_{ET} . The calculated η_{ET} for the samples doped with 1%, 5%, 12%, 15% and 18mol% Yb^{3+} , which are 30.7%, 41.5%, 45.3%, 61.5% and 67.8%, respectively.

It is well known that the efficiency of energy transfer from Ho^{3+} to Yb^{3+} can usually be obtained based on the variation of the lifetime of the $^5\text{F}_4$, $^5\text{S}_2$ state of Ho^{3+} in the Ho^{3+} singly doped and $\text{Ho}^{3+}/\text{Yb}^{3+}$ co-doped samples. To verify the validity of the new method, the luminescence decay curves of the Ho^{3+} : $^5\text{F}_4$, $^5\text{S}_2 \rightarrow ^5\text{I}_8$ (556 nm) emission in $\text{BaZr}_{0.7}\text{Y}_{0.2-x}\text{O}_{3-\delta}$: 10% Ho^{3+} with different Yb^{3+} concentration were also measured on the excitation at the Ho^{3+} : $^5\text{G}_6$ level (455 nm), shown in **Fig. 6**. The decrease of the lifetime for the Ho^{3+} 556 nm emission with the increase of the Yb^{3+} doping concentration also proves the energy transfer from Ho^{3+} to Yb^{3+} . The average lifetime (τ) of the $^5\text{F}_4$, $^5\text{S}_2$ state of Ho^{3+} and the energy transfer efficiency (η'_{ET}) can be calculated by using the following equations[35, 36]

$$\tau = \frac{\int_0^{\infty} tI(t)dt}{\int_0^{\infty} I(t)dt}, \quad (4)$$

$$\eta'_{\text{ET}} = 1 - \tau_{x\%}/\tau_0. \quad (5)$$

Here $I(t)$ is the time-dependent luminescence intensity, $\tau_{x\%}$ and τ_0 are the average lifetime of the $^5\text{F}_4$, $^5\text{S}_2$ state of Ho^{3+} with $x\%\text{Yb}^{3+}$ and without Yb^{3+} doping, respectively. With Eq. (5), it has been calculated that the energy transfer efficiency for the samples doped with 1, 5, 12, 15 and 18mol% Yb^{3+} are 36.5%, 47.6%, 52.8%, 56.6% and 60.2%, respectively. The energy transfer efficiencies as function of Yb^{3+} concentration calculated with different methods are both shown in **Fig. 7 (a)**. It is found that energy transfer efficiency calculated with luminescence intensity ratio is very close to that with the lifetime-variation. The errors of values of energy transfer efficiency based on luminescence intensity ratio method might originate in the slight inconsistency of test condition during the measurement process. The result suggests that the method based on luminescence intensity ratio is also valid to roughly estimate the energy transfer efficiency.

Fig. 6 Luminescence decay curves of the $\text{Ho}^{3+}: {}^5\text{F}_4, {}^5\text{S}_2 \rightarrow {}^5\text{I}_8$ (556 nm) emission in $\text{BaZr}_{0.7}\text{Y}_{0.2-x}\text{O}_{3-\delta}$: 10% Ho^{3+} with different Yb^{3+} concentration under excitation of 455 nm.

Fig. 7 Efficiency tendency of energy transfer from Ho^{3+} to Yb^{3+} ions when changing Yb^{3+} concentration for $\text{BaZr}_{0.7}\text{Y}_{0.2-x\%}\text{O}_{3-\delta}$: 10% Ho^{3+} , x% Yb^{3+} . The energy transfer efficiency is calculated based on lifetime variation (a) and luminescence intensity ratio (b), respectively.

Fig. 8 Tendency of ratio between the total energy transfer efficiency and non-radiative transfer efficiency when changing Yb^{3+} concentration for $\text{BaZr}_{0.7}\text{Y}_{0.2-x\%}\text{O}_{3-\delta}$: 10% Ho^{3+} , x% Yb^{3+}

The total energy transfer QC for near infrared emission depends on not only the energy transfer efficiency (η_{ET}) but also the back energy transfer efficiency (η_{BET}). Moreover, the non-radiative process from the $^5\text{F}_4$, $^5\text{S}_2 \rightarrow ^5\text{I}_6$ of Ho^{3+} that can populate the $^5\text{I}_6$ level also contributes to the near infrared luminescence. Thus it is difficult to calculate the total QC. By comparing the intensity ratios of the 1216 nm of the $\text{Ho}^{3+}/\text{Yb}^{3+}$ co-doped and Ho^{3+} singly doped samples under 455nm excitation, however,

we can still further know the properties of the Yb^{3+} concentration dependent total QC near infrared emission. The measured intensity at 1216 nm corresponding to the $\text{Ho}^{3+}:^5\text{I}_6 \rightarrow ^5\text{I}_8$ transition at different Yb^{3+} concentration is expressed as

$$I'_{x\% \text{Yb}} = kh\nu_{\text{NIR}}(\eta_N + \eta_{\text{ET}} + \eta_{\text{ET}}\eta_{\text{BET}})N. \quad (6)$$

Where ν_{NIR} is the frequency of the 1216 nm emission of Ho^{3+} , η_N is the efficiency of non-radiative process from the $^5\text{F}_4(^5\text{S}_2) \rightarrow ^5\text{I}_6$. The 1216 nm emission intensity ratio R_0 between $\text{Yb}^{3+}/\text{Ho}^{3+}$ co-doped and Ho^{3+} singly doped sample is then written as

$$R_0 = I'_{x\% \text{Yb}}/I'_{0\% \text{Yb}} = [kh\nu_{\text{NIR}}(\eta_N + \eta_{\text{ET}} + \eta_{\text{ET}}\eta_{\text{BET}})N]/kh\nu_{\text{NIR}}\eta_N N. \quad (7)$$

Where $I'_{0\% \text{Yb}}$ and $I'_{x\% \text{Yb}}$ are the 1216 nm luminescence intensity of Ho^{3+} in the absence and presence of Yb^{3+} ($x=1, 5, 12, 15, 18$), respectively. Thus the ratio (S) between the total energy transfer QC and the non-radiative efficiency for the near infrared emission can be expressed as

$$S = (\eta_{\text{ET}} + \eta_{\text{ET}}\eta_{\text{BET}})/\eta_N = I'_{x\% \text{Yb}}/I'_{0\% \text{Yb}} - 1. \quad (8)$$

The S value as a function of Yb^{3+} concentration is shown in **Fig. 8**. It is found that energy transfer QC becomes a dominate route performing the near infrared emission with Yb^{3+} concentration increasing. With Eq. (8), it is easy to know that almost 90% of 1216 nm emission is caused by the energy transfer QC at Yb^{3+} concentration of 12%. However, the total energy transfer QC tends to decrease when the Yb^{3+} concentration is higher than 12%. Since the energy transfer efficiency always increases with Yb^{3+} concentration increasing, the lowered total energy transfer QC may ascribed the decreased back energy transfer efficiency because the concentration quenching among Yb^{3+} ions is inevitable at high Yb^{3+} concentration. The result

indicates that the Yb^{3+} ions are impossible to wholly transfer their accepted energy back to Ho^{3+} ions, especially at high Yb^{3+} concentration, discounting the actual QC efficiency for the near infrared emission.

4. Conclusions

In this work, $\text{Ho}^{3+}/\text{Yb}^{3+}$ co-doped $\text{BaZr}_{0.8}\text{Y}_{0.2}\text{O}_{3-\delta}$ phosphors have been synthesized via a co-precipitation method. The performance and mechanism of the QC near infrared emission caused by energy transfer have been investigated. All the samples present very weak Yb^{3+} emission due to the efficient $\text{Yb}^{3+} \rightarrow \text{Ho}^{3+}$ back energy transfer. Therefore, it is possible to obtain pure near infrared emission of Ho^{3+} in the $\text{Ho}^{3+}/\text{Yb}^{3+}$ co-doped $\text{BaZr}_{0.8}\text{Y}_{0.2}\text{O}_{3-\delta}$. The optimum sample for near infrared emission is $\text{BaZr}_{0.7}\text{Y}_{0.08}\text{O}_{3-\delta}$: 0.12Yb^{3+} , 0.1Ho^{3+} , in which the energy transfer from Ho^{3+} to Yb^{3+} is 52.8% and 90% of near infrared emission is performed by the energy transfer induced QC. This research may provide meaningful reference for designing efficient new photonic devices.

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