Color-tunable luminescence, energy transfer and temperature sensing behavior of hexagonal NaYF₄:Ce³⁺/Tb³⁺/Eu³⁺ microcrystals

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Abstract

In this paper, a series of color-tunable phosphors from green to yellow and eventually to red have been successfully synthesized with efficient Ce³⁺ → Tb³⁺ → Eu³⁺ energy transfer in hexagonal NaYF₄ host. The energy transfer processes from Ce³⁺ to Tb³⁺ and from Tb³⁺ to Eu³⁺ and the corresponding energy transfer efficiencies are carefully investigated by the photoluminescence excitation spectra, emission spectra and the decay curves. Impressively, the Ce³⁺ → Tb³⁺ → Eu³⁺ energy transfer mechanism has been proposed and can be attributed to the strong absorption of ultraviolet light by sensitizers (Ce³⁺), followed by energy migration to Tb³⁺ ions, from which the energy is finally transferred to activators (Eu³⁺). Furthermore, the temperature sensing behavior of β-NaYF₄:Ce³⁺/Tb³⁺/Eu³⁺ under 248 nm ultraviolet light excitation is also studied to explore the possible application of the as-synthesized sample in optical thermometry. Evidently, the results suggest that the investigated β-NaYF₄:Ce³⁺/Tb³⁺/Eu³⁺ sample may be a promising candidate for optical temperature sensor.

Keywords: Energy transfer, color-tunable luminescence, temperature sensing behavior

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1. Introduction

Currently, lanthanide (Ln^{3+}) ions doped inorganic luminescent materials have been widely investigated for their potential applications in various fields such as white light-emitting diodes (LEDs), solid-state lasers, solar cells, anti-counterfeiting, volumetric three-dimensional displays, sensors, biological labels, multimodal bioimaging and drug delivery[1-9]. In order to realize favorable optical performance, the host materials, where Ln^{3+} ions reside, should be appropriately selected, because the radiative and nonradiative transitions as well as energy transfer of Ln^{3+} ions are highly dependent on the crystalline field surrounding them. Till now, large number of rare earth inorganic compounds, including oxides[10, 11], oxysulfides[12, 13], oxyfluorides[14, 15], sulfides[16], fluorides[17-19], chlorides[20, 21], phosphates[22] and vanadates[23], have been selected as host materials for the doping of rare earth ions. Among the as-reported host materials, Ln^{3+} -doped fluorides with general formula NaLnF_4 , possessing low phonon energy, good optical transparency and adequate thermal and environmental stability, have been regarded as excellent host lattices for achieving desirable optical performance. Especially, hexagonal NaYF_4 ($\beta\text{-NaYF}_4$) is well known as one of the most efficient hosts for performing multicolor down-conversion (DC) and up-conversion (UC) luminescence of Ln^{3+} ions[24].

As we all know, the luminescence of Ln^{3+} -doped materials originates primarily from electronic transitions within the $4f^N$ configuration of the doped lanthanide ions[25]. To precisely control the optical emission, the trivalent lanthanide ions including Eu^{3+} , Tb^{3+} , Sm^{3+} and Dy^{3+} are usually selected to be doped into the host lattice. Specially, Tb^{3+} and Eu^{3+} ions are generally regarded as green-emission and red-emission activators owing to the $^5\text{D}_4 \rightarrow ^7\text{F}_J$ ($J = 4, 3, 2, 1$) transitions of Tb^{3+} and the $^5\text{D}_0 \rightarrow ^7\text{F}_J$ ($J = 6, 5, 4, 3$) transitions of Eu^{3+} [26]. Compared with the single-doping models, sensitizers and activators co-doped systems exhibit more efficient luminescence because of the high absorption coefficient and efficient energy transfer from sensitizers to activators. Ce^{3+} ions with 4f-5d allowed transition are usually selected as sensitizer to improve the luminescent performance of the activators (*e. g.* Tb^{3+} and Eu^{3+}) with 4f-4f forbidden transitions[27]. However, direction sensitization

of Eu^{3+} ions by Ce^{3+} ions is not applicable due to the existence of competing metal-metal charge transfer (*e. g.* $\text{Ce}^{3+} + \text{Eu}^{3+} \rightarrow \text{Ce}^{4+} + \text{Eu}^{2+}$), which seriously quenches the luminescence of Ce^{3+} and Eu^{3+} ions[28, 29]. Subsequently, Tb^{3+} ions are found to act as a bridge between Ce^{3+} and Eu^{3+} to minimize the metal-metal charge transfer and maximize the energy transfer rate, resulting in strong green and/or red emissions under broadband near-ultraviolet excitation through $\text{Ce}^{3+} \rightarrow (\text{Tb}^{3+})_n \rightarrow \text{Eu}^{3+}$ (n represents the number of Tb^{3+} ions in a representative energy migration chain) energy hopping process. Despite the above advances, the $\text{Ce}^{3+} \rightarrow \text{Tb}^{3+} \rightarrow \text{Eu}^{3+}$ energy transfer in $\beta\text{-NaYF}_4$ host and the luminescent properties of $\beta\text{-NaYF}_4\text{:Ce}^{3+}/\text{Tb}^{3+}/\text{Eu}^{3+}$ has been rarely reported.

In the present work, we report the color-tunable emission, energy transfer and temperature sensing behavior of $\text{Ce}^{3+}/\text{Tb}^{3+}/\text{Eu}^{3+}$ co-doped $\beta\text{-NaYF}_4$ microcrystals. Through varying the molar ratio of $\text{Ce}^{3+}/\text{Tb}^{3+}/\text{Eu}^{3+}$ in $\beta\text{-NaYF}_4$ host, efficient green-yellow-red color-tunable emission can be generated from the as-synthesized $\beta\text{-NaYF}_4\text{:Ce}^{3+}/\text{Tb}^{3+}/\text{Eu}^{3+}$ with an effective absorption in the ultraviolet range, including a ultraviolet band originating from Ce^{3+} ions and green, red lines from Tb^{3+} and Eu^{3+} , respectively. The luminescent properties of Ce^{3+} , Tb^{3+} and/or Eu^{3+} co-doped $\beta\text{-NaYF}_4$ samples are systemically investigated and the corresponding energy transfer mechanism is also discussed in detail. More importantly, the temperature sensing behavior of $\beta\text{-NaYF}_4\text{:Ce}^{3+}/\text{Tb}^{3+}/\text{Eu}^{3+}$ has been studied for the first time, as far as we know.

2. Experimental Section

2.1 Materials

As starting materials, the rare earth chlorides $\text{RECl}_3 \cdot 6\text{H}_2\text{O}$ (99.99%) ($\text{RE} = \text{Y}, \text{Eu}, \text{Tb}$), $\text{CeCl}_3 \cdot 7\text{H}_2\text{O}$ (99.99%) were purchased from Beijing Founde Star Science & Technology Co., Ltd (China). NaF (98%) and sodium citrate (99%) were supplied by Sinopharm Chemical Reagent Co., Ltd (China). Deionized water was used throughout. All chemicals are of analytical grade reagents and used directly without further purification.

2.2 Synthesis

In a typical procedure for preparing β -NaYF₄ microcrystals, 2 mmol YCl₃·6H₂O were firstly dissolved in 10 mL deionized water with magnetic stirring to form yttrium chloride solution. Then 20 mL aqueous solution containing 2 mmol trisodium citrate was added into the resulting solution to form the metal-citrate complex. After vigorous stirring for 30 min, 30 mL of NaF aqueous solution (0.8 mol/L) was dropped into the above solution under thoroughly stirring for 15 min. Subsequently, the as-obtained mixing solution was transferred into a Teflon bottle held in a stainless steel autoclave, and heated at 220 °C for 12 h. After the autoclave was cooled down to room temperature naturally, the precipitates were collected by centrifugation, washed with deionized water and ethanol in sequence. Then the collected samples were dried in air at 80 °C for 12 h.

2.3 Characterization

X-ray powder diffraction (XRD) measurements were performed on a ARL X'TRA diffractometer at a scanning rate of 10° min⁻¹ in the 2 θ range from 10° to 80° with Cu K α radiation (λ = 0.15406 nm). The morphology of the samples was inspected by a field emission scanning electron transmission microscope (FE-SEM, SU8010, Hitachi). The photoluminescence (PL) excitation and emission spectra, luminescence decay curves were recorded with an Edinburgh Instruments FS5 fluorescence spectrophotometer. The temperature dependent emission spectra were detected on the Edinburgh Instruments FS5 fluorescence spectrophotometer equipped with a homemade temperature controlling stage.

3. Results and Discussion

3.1 Crystal phase and morphology

Fig.1 shows the XRD patterns of the as-synthesized NaYF₄, NaYF₄:Ce³⁺, NaYF₄:Ce³⁺/Tb³⁺ and NaYF₄:Ce³⁺/Tb³⁺/Eu³⁺ samples as well as the standard data of pure hexagonal NaYF₄ (β -NaYF₄). As shown, all the samples exhibit similar XRD patterns and all the diffraction peaks of these products can be well indexed to the hexagonal-phase NaYF₄, which are in good agreement with the standard card (JCPDS No. 28-1192). The crystal structure of hexagonal NaYF₄ is determined with lattice parameters of a = 0.596 nm and c = 0.353 nm, space group P6₃/mmc[30]. No impurity

peaks are observed in all the XRD patterns, indicating that the dopant ions (Ce^{3+} , Eu^{3+} and Tb^{3+}) are completely dissolved in the host lattice with little effect on the crystallinity or phase change because of their almost same ionic radii and identical valence. To provide further insight into the as-obtained products, SEM investigation and EDS analysis are also performed, as shown in Fig. 2. The representative FE-SEM images in Fig. 2a and Fig. 2b reveal that the as-obtained $\beta\text{-NaYF}_4\text{:10\%Ce}^{3+}$, $\text{30\%Tb}^{3+}$, $\text{1\%Eu}^{3+}$ sample consists of uniform hexagonal microplates with average size of $3.2\ \mu\text{m}$ in width and $1.2\ \mu\text{m}$ in thickness. From the magnified SEM image in Fig. 2c and Fig. 2d, we can clearly see the hexagonal plate-like structure of the sample. The EDS spectrum (Fig. 2e) is adopted to confirm the presence of Na, Y, Ce, Tb, Eu and F elements, also indicating that Ce^{3+} , Tb^{3+} and Eu^{3+} ions can be thoroughly doped into hexagonal NaYF_4 host lattice.

3.2 Photoluminescence properties

Photoluminescence excitation (PLE) and photoluminescence (PL) spectra of Ce^{3+} , $\text{Ce}^{3+}/\text{Tb}^{3+}$ and $\text{Ce}^{3+}/\text{Tb}^{3+}/\text{Eu}^{3+}$ doped $\beta\text{-NaYF}_4$ samples are presented in Fig. 3. The PLE spectrum of the $\beta\text{-NaYF}_4\text{:10\%Ce}^{3+}$ sample clearly demonstrates that there is a broad absorption band peaked at 248 nm, which is assigned to the $4f \rightarrow 5d$ transition of Ce^{3+} (left line, Fig. 3a). Under the excitation of near-ultraviolet with 248 nm wavelength from the characteristic absorption peak of Ce^{3+} , the emission spectrum consists of a broadband emission with a maximum at about 298 nm, which results from the electric-dipole-allowed $4f\text{-}5d$ transition of Ce^{3+} ions (right line, Fig. 3a; Fig. 3b)[31]. Fig. 3c presents the excitation and emission spectra of $\beta\text{-NaYF}_4\text{:10\%Ce}^{3+}$, $\text{30\%Tb}^{3+}$ product. Obviously, in Ce^{3+} , Tb^{3+} co-doped $\beta\text{-NaYF}_4$, the excitation spectrum for Tb^{3+} emission (542 nm) is dominated by the strong and broad absorption band peaked at around 248 nm due to the Ce^{3+} : $4f \rightarrow 5d$ transition, revealing that the existence of energy transfer from Ce^{3+} ions to Tb^{3+} ions (left line, Fig. 3c). Excitation into the $4f\text{-}5d$ transition of Ce^{3+} at 248 nm yields four obvious sharp lines centered at 486, 542, 580 and 621 nm, which can be ascribed to the $^5\text{D}_4 \rightarrow ^7\text{F}_J$ ($J = 6, 5, 4$ and 3) characteristic transitions of Tb^{3+} ions (right line, Fig. 3d; Fig. 3e)[32]. To investigate the energy transfer ($\text{Ce}^{3+} \rightarrow \text{Tb}^{3+} \rightarrow \text{Eu}^{3+}$) process, the PLE and PL spectra of

β -NaYF₄: 10%Ce³⁺, 30%Tb³⁺, 10%Eu³⁺ are also depicted in Fig. 3f. By monitoring the 614 nm red emission of Eu³⁺ ions, the excitation spectrum (left line, Fig. 3f) of the Ce³⁺/Tb³⁺/Eu³⁺ co-doped β -NaYF₄ sample is recorded and similar to that of β -NaYF₄: Ce³⁺/Tb³⁺, indicating the successful sensitization of Eu³⁺ emission via Ce³⁺ $\rightarrow$ Tb³⁺ $\rightarrow$ Eu³⁺ energy transfer in β -NaYF₄: Ce³⁺/Tb³⁺/Eu³⁺ system. Upon Ce³⁺ excitation at 248 nm, the as-synthesized sample exhibits strong Eu³⁺: ⁵D₀ $\rightarrow$ ⁷F_J (J = 1, 2 and 4) red emission peaks at 590, 614 and 691 nm, while the emissions of Ce³⁺ and Tb³⁺ suffer from obvious quenching (right line, Fig. 3f)[33]. The above results powerfully demonstrate that the efficient energy transfer from Ce³⁺ to Eu³⁺ has successfully realized in β -NaYF₄: Ce³⁺/Tb³⁺/Eu³⁺ system by selecting Ce³⁺, Tb³⁺ and Eu³⁺ as sensitizer, migrator and activator, respectively. With the help of Tb³⁺ as a bridge, Ce³⁺ can transfer its excitation energy to Eu³⁺ through Ce³⁺ $\rightarrow$ Tb³⁺ $\rightarrow$ Eu³⁺ energy migration process (Fig. 3g).

To further investigate the energy transfer process between Ce³⁺ and Tb³⁺, a series of Ce³⁺/Tb³⁺ co-doped β -NaYF₄ samples were successfully synthesized. Fig. 4a shows the PL spectra of β -NaYF₄:10%Ce³⁺, x%Tb³⁺ (x = 0, 10, 15, 30, 40 and 50) products, in which the insets reveal the dependence of Tb³⁺ emission intensity and the Ce³⁺ $\rightarrow$ Tb³⁺ energy transfer efficiencies on the dopant concentration of Tb³⁺ ions. Under excitation at 248 nm, both ultraviolet broadband emission of Ce³⁺ and green sharp emission peaks of Tb³⁺ can be clearly observed. As the Tb³⁺ concentration increases, the emission intensity of Ce³⁺ decreases gradually, whereas the Tb³⁺ emission intensity increases initially and begins to decrease at x > 15 (Fig. S1 and Fig. 4b). The energy transfer efficiency (η_{Ce-Tb}) of Ce³⁺ $\rightarrow$ Tb³⁺ can be calculated by the following equation[34]

$$\eta_{Ce-Tb} = 1 - \frac{I}{I_0} \quad (1)$$

Where I and I_0 represent the luminescence intensity of Ce³⁺ in the absence and in the presence of Tb³⁺, respectively. The Ce³⁺ $\rightarrow$ Tb³⁺ energy transfer efficiency in β -NaYF₄:10%Ce³⁺, x%Tb³⁺ samples is calculated and presented in Fig. 4c. As shown, the transfer efficiency increases monotonously with the increasing of Tb³⁺ content

from $x = 0$ to 50, and the maximum value of η_{Ce-Tb} is estimated to be 96.0% at $x = 50$, strongly evidencing that $Ce^{3+} \rightarrow Tb^{3+}$ energy transfer occurs in β -NaYF₄ host. With the increment of Tb^{3+} content, the distance between the sensitizer (Ce^{3+}) and the activator (Tb^{3+}) becomes shorter, which is conducive to the efficient energy transfer ($Ce^{3+} \rightarrow Tb^{3+}$), leading to the decrease of Ce^{3+} emission intensity and enhancement of Tb^{3+} emission. However, with further increase of Tb^{3+} content, the distance between Tb^{3+} ions could also shorten, resulting that the probability of energy transfer among Tb^{3+} ions becomes greater. Eventually, the occurrence of Tb^{3+} - Tb^{3+} internal concentration quenching will result in the decrease of Tb^{3+} emission intensity. As observed by naked eyes, all these samples exhibit green emission under 254 nm ultraviolet lamp (insets in Fig. 4), corresponding to the chromaticity coordinates in the Commission International de l'Eclairage (CIE) 1931 chromaticity diagram (Fig. S2 and Table S1). Furthermore, the green emission intensity of β -NaYF₄:10% Ce^{3+} , 15% Tb^{3+} is the strongest, agreeing well with the results of emission spectra.

In the $Ce^{3+} \rightarrow Tb^{3+} \rightarrow Eu^{3+}$ energy transfer progress, the dopant concentration of Tb^{3+} should be larger than that of Eu^{3+} so as to maximize the energy transfer versus metal-metal charge transfer quenching. By referring to the previous work of J. Shi and X. Zhang et al., the Tb^{3+} concentration in β -NaYF₄: Ce^{3+} / Tb^{3+} / Eu^{3+} system can be set as 30 mol%, which can not only form a $Ce^{3+} \rightarrow Tb^{3+} \rightarrow Eu^{3+}$ energy transfer chain but also avoid the waste of terbium chloride because of its high price[32, 33]. Furthermore, the low content of Eu^{3+} may induce to an incomplete energy transfer from Tb^{3+} to Eu^{3+} , subsequently resulting in low luminescent efficiency and inferior color purity. In order to optimize the dopant concentration of Eu^{3+} ions and obtain color-tunable luminescence, the PL spectra of β -NaYF₄: 10% Ce^{3+} , 30% Tb^{3+} , $y\%Eu^{3+}$ ($y = 0, 0.5, 1, 2, 3, 5, 10$ and 20) samples are shown in Fig. 5a. As Eu^{3+} content increases, the emission intensity of Tb^{3+} decreases gradually, whereas the emission intensity of Eu^{3+} ions simultaneously increases, reaching a maximum value at $y = 2$, and then decreases with further increasing Eu^{3+} content (Fig. S3 and Fig. 5b). The energy transfer efficiency (η_{Tb-Eu}) from Tb^{3+} to Eu^{3+} can be calculated by[35]

$$\eta_{Tb-Eu} = 1 - \frac{I_1}{I_2} \quad (2)$$

in which I_1 and I_2 denote the emission intensities of Tb^{3+} ions with and without Eu^{3+} ions, respectively. Fig. 5c shows the $Tb^{3+} \rightarrow Eu^{3+}$ energy transfer efficiency of $\beta\text{-NaYF}_4\text{:}10\%\text{Ce}^{3+}$, $30\%\text{Tb}^{3+}$, $y\%\text{Eu}^{3+}$ samples as a function of Eu^{3+} concentration. The energy transfer efficiency η_{Tb-Eu} is found to increase gradually with the increment of Tb^{3+} concentration and saturate at $y = 5$ ($\sim 96\%$), indicating that high content of Tb^{3+} ions is beneficial for blocking the metal-metal charge transfer between Ce^{3+} and Eu^{3+} and realizing an efficient energy transfer from Tb^{3+} and Eu^{3+} (Fig. 5c).

Generally, the energy transfer from Tb^{3+} to Eu^{3+} is ascribed to multipolar interaction between donor and acceptor ions. The energy transfer probability through multipolar interaction can be described as follows[36]

$$P(R) \propto \frac{Q_A}{R^b \tau_D} \int \frac{f_D(E)F_A(E)}{E^c} dE \quad (3)$$

Where P represents the energy transfer probability, τ_D denotes the decay time of donor emission, Q_A is the total absorption cross-section of acceptor, and R is the distance between donor and acceptor; b and c are parameters that depend on the type of energy transfer. Based on this equation, the energy transfer probability (P) is inversely proportional to decay time (τ_D). In other words, the luminescent lifetime of sensitizer is obviously shortened in the case of energy transfer process, owing to the occurrence of additional channels that can shorten the lifetime of the excited state. So, to further validate the $Tb^{3+} \rightarrow Eu^{3+}$ energy transfer in $\beta\text{-NaYF}_4\text{:Ce}^{3+}/\text{Tb}^{3+}/\text{Eu}^{3+}$ microcrystals, the decay lifetimes of Tb^{3+} in $\beta\text{-NaYF}_4\text{:Ce}^{3+}/\text{Tb}^{3+}/\text{Eu}^{3+}$ samples are measured and provided in Fig. 6a. Owing to the non-single-exponential decay feature in the donor-acceptor energy transfer system, the effective experimental lifetime can be defined as[37]

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

where $I(t)$ denotes the luminescent intensity at time t . Apparently, as the Eu^{3+} dopant content increased, the obtained lifetime of Tb^{3+} emission decreases continuously from 4.06 ms at $y = 0$ to 0.92 ms at $y = 20$ (Fig. 6b), powerfully confirming the existence of the efficient energy transfer process from Tb^{3+} to Eu^{3+} . The luminescent decay curves

of Eu^{3+} ions in $\beta\text{-NaYF}_4\text{:10\%Ce}^{3+}, 30\%\text{Tb}^{3+}, y\%\text{Eu}^{3+}$ ($y = 0.5 \sim 20$) products are also measured and presented in Fig. 6c. As shown, the average lifetime of Eu^{3+} decreases slightly with rising Eu^{3+} concentration ($y = 0.5 \sim 3$), and then decreases greatly from $y = 3$ to $y = 20$ (Fig. 6d). Remarkably, the decay time of Eu^{3+} emission begins to decrease suddenly at a certain dopant concentration (defined as critical concentration), which can be attributed to the concentration quenching behavior. According to the Dexter and Schulman's theory, concentration quenching phenomenon is caused by the nonradiative energy transfer between activators, which can shorten the lifetime of the excited states[38]. When the dopant content of Eu^{3+} is higher than or equal to the critical concentration, the distance among Eu^{3+} ions becomes shorter, which induces to the increase of nonradiative rate of Eu^{3+} ions, resulting in the decrease of Eu^{3+} decay lifetime.

In the $\text{Ce}^{3+} \rightarrow \text{Tb}^{3+} \rightarrow \text{Eu}^{3+}$ energy transfer chain, the energy transfer from Tb^{3+} to Eu^{3+} may occur through exchange interaction and/or electric multipole interaction, which depends on the average distance between Eu^{3+} and Tb^{3+} ions. In general, the exchange interaction requires an overlap of the donor's and acceptor's orbits, and therefore the value of average distance should be less than 7 Å. Otherwise, the electric multipole interaction could be dominate in this energy transfer process.[35, 39] To distinguish which interaction plays a leading role, the critical distance (R_c) is utilized to act as an assumption for efficient $\text{Ce}^{3+} \rightarrow \text{Tb}^{3+} \rightarrow \text{Eu}^{3+}$ energy transfer and can be estimated from the following equation[40, 41]

$$R_c = 2\left[\frac{3V}{4\pi CN}\right]^{1/3} \quad (5)$$

where C denotes the total concentrations of Ce^{3+} , Tb^{3+} and Eu^{3+} ions, V is the cell volume of $\beta\text{-NaYF}_4$, and N represents the number of host cations in the unit cell. As for hexagonal NaYF_4 , the values of V and N are found to be 108.59 (Å³) and 1.5, respectively. When the concentrations of Ce^{3+} and Tb^{3+} ions are fixed to 10 mol% and 30 mol%, calculations with increasing Eu^{3+} concentration ($y = 0.5, 1, 2, 3, 5, 10$ and 20) yield $R = 6.98, 6.96, 6.90, 6.85, 6.74, 6.51$ and 6.13 Å for $C = 0.405, 0.41, 0.42, 0.43, 0.45, 0.5$ and 0.6, respectively. Obviously, these calculated values are all smaller

than the critical distance (7 Å) required for the exchange interaction mechanism, indicating that the $\text{Tb}^{3+} \rightarrow \text{Eu}^{3+}$ energy transfer occurs via the exchange interaction.

It is found that the emission colors of $\beta\text{-NaYF}_4\text{:Ce}^{3+}/\text{Tb}^{3+}/\text{Eu}^{3+}$ samples can be precisely tuned by changing the dopant content of Eu^{3+} ions because of the efficient $\text{Ce}^{3+} \rightarrow \text{Tb}^{3+} \rightarrow \text{Eu}^{3+}$ energy transfer. To visualize the Eu^{3+} doping-induced emission color modification, the CIE chromaticity coordinates (calculated according to the relevant PL spectra) and corresponding luminescent photographs for the $\beta\text{-NaYF}_4\text{:10%Ce}^{3+}, 30\%\text{Tb}^{3+}, y\%\text{Eu}^{3+}$ ($y = 0 \sim 20$) phosphors are provided in Fig. 7 and Table S2. Obviously, with the increasing Eu^{3+} concentration from 0 mol% to 20 mol%, the emission colors can be finely tuned from pure green (0.3415, 0.5720) to yellow (0.4993, 0.4506) and finally to red (0.4113, 0.3228), as evidenced by the variation of chromaticity coordinates in CIE chromaticity diagram.

Based on the above discussion, a possible scheme of $\text{Ce}^{3+} \rightarrow \text{Tb}^{3+} \rightarrow \text{Eu}^{3+}$ energy transfer in $\beta\text{-NaYF}_4$ host has been proposed and presented in Fig. 8[28, 29]. Upon the ultraviolet excitation ($\lambda = 248$ nm), the electrons Ce^{3+} ions can be effectively excited from the ground state ($^2\text{F}_{5/2}$) to the 5d excited state and subsequently return to the lowest vibrational level of the excited state via nonradiative relaxation process. When some of these electrons return back to the ground states ($^2\text{F}_{7/2}$ and $^2\text{F}_{5/2}$), near ultraviolet emission at 298 nm, resulting from the electric-dipole-allowed 4f-5d transition of Ce^{3+} , can be clearly observed. Simultaneously, other excited electrons return from the 5d excited states to ground states through a nonradiative energy transfer process to the $^5\text{D}_3$ level of Tb^{3+} ions owing to their similar energy levels, followed by nonradiative relaxation to the $^5\text{D}_4$ level of Tb^{3+} ions. Then the electrons remove from the $^5\text{D}_4$ excited state to the $^7\text{F}_J$ ($J = 3, 4, 5$ and 6) ground state, resulting in the green emission of Tb^{3+} ions. With the addition of Eu^{3+} ions in $\beta\text{-NaYF}_4\text{:Ce}^{3+}/\text{Tb}^{3+}$ system, the $\text{Tb}^{3+} \rightarrow \text{Eu}^{3+}$ energy transfer generally occurs in the following two ways: (i) energy transfer takes place from the 4f-4f transition of Tb^{3+} at high energy levels to the next level 4f-4f transition of Eu^{3+} excited states (*e. g.* excitation energy of $^5\text{D}_4$ level (Tb^{3+}) transfers to $^5\text{D}_1$ level of Eu^{3+}); (ii) Cross-relaxation process happens between the $^7\text{F}_0$ level of Eu^{3+} ions and $^5\text{D}_3$ level of

Tb³⁺ ions, which can be described as follows:

Either way, the excited energy can be nonradiatively transferred to the ⁵D₀ metastable state of Eu³⁺ ions and finally the red emission of Eu³⁺ ions is obtained as a result of ⁵D₀ → ⁷F_J (J = 0, 1, and 2) transitions.

3.3 Temperature sensing behavior

Eventually, the temperature-dependent luminescent behavior of β-NaYF₄:Ce³⁺/Tb³⁺/Eu³⁺ under 248 nm ultraviolet light excitation has been investigated in order to explore the possible application of the current samples in optical thermometry. The temperature dependent emission spectra of β-NaYF₄:10%Ce³⁺, 30%Tb³⁺, 0.5%Eu³⁺ from 303 K to 573 K are illustrated in Fig. 9a. As shown, the luminescent intensities of both Tb³⁺ and Eu³⁺ all decrease gradually as the temperature increases due to the thermal activation of nonradiative-decay pathways. To further exhibit the variation of the relative emission intensity ratio, all the luminescent spectra are normalized to the 614 nm emission band of Eu³⁺: ⁵D₀ → ⁷F₂ transition, as presented in Fig. 9b. The luminescent intensity ratio (defined as FIR) between the Tb³⁺: ⁵D₄ → ⁷F₅ (*I_{Tb}*) transition and the Eu³⁺: ⁵D₀ → ⁷F₂ transition (*I_{Eu}*) is adopted to investigate the temperature-dependent luminescence. Interestingly, for Ce³⁺, Tb³⁺ and Eu³⁺ co-doped β-NaYF₄ sample, the FIR (*I_{Eu}/I_{Tb}*) value monotonically decreases with the increment of temperature from 300 K to 573 K, which can be ascribed to the enhanced energy transfer from Tb³⁺ to Eu³⁺[42, 43]. With increasing temperature, the electrons in the excited state of Tb³⁺ ions may nonradiatively transfer their energy to the excited state of Eu³⁺ through thermal activation, from which the Eu³⁺ emissions happen. Consequently, the energy transfer from Tb³⁺ to Eu³⁺ in hexagonal NaYF₄ host enhances gradually with the increase of temperature, resulting in the monotonous decrease of FIR value. To obtain the sensitivity of β-NaYF₄:Ce³⁺/Tb³⁺/Eu³⁺ sample for temperature sensing, the temperature-dependent FIR can be linearly fitted by the following equation from 300 K to 573 K

$$FIR = \frac{I_{Eu}}{I_{Tb}} = 3.55 - 0.0046T \quad (6)$$

As shown in Fig. 9c, the sensitivity of the β -NaYF₄:Ce³⁺/Tb³⁺/Eu³⁺ sample is about 0.46% per K, suggesting that β -NaYF₄:Ce³⁺/Tb³⁺/Eu³⁺ system is suitable to be used as luminescent thermometer at this temperature range. Remarkably, the reusability of this temperature sensor is quite good after several cycle experiments. The above results strongly demonstrate that the investigated β -NaYF₄:Ce³⁺/Tb³⁺/Eu³⁺ phosphors is a quite promising candidate for the application in optical temperature sensors.

4. Conclusion

In conclusion, a series of Ce³⁺, Tb³⁺ co-doped and Ce³⁺, Tb³⁺, Eu³⁺ tri-doped β -NaYF₄ hexagonal microplates with remarkably uniform morphology and size have been successfully synthesized by a facile hydrothermal method. The energy transfer processes of Ce³⁺ → Tb³⁺ and Tb³⁺ → Eu³⁺ are systematically investigated to realize the terbium bridge to overcome metal-metal charge transfer quenching between Ce³⁺ and Eu³⁺, resulting in intense green emission of Tb³⁺ and red emission of Eu³⁺ in β -NaYF₄:Ce³⁺/Tb³⁺/Eu³⁺ samples upon the allowed Ce³⁺: 4f-5d electronic transition excitation. By properly controlling the Ce³⁺/Tb³⁺/Eu³⁺ ratio in hexagonal NaYF₄ host, efficient green-yellow-red color-tunable emission can be obtained via the Ce³⁺ → Tb³⁺ → Eu³⁺ energy transfer process. Moreover, the temperature-dependent luminescent behavior of β -NaYF₄:Ce³⁺/Tb³⁺/Eu³⁺ demonstrates that the fluorescent intensity ratio between the Tb³⁺: ⁵D₄ → ⁷F₅ transition and the Eu³⁺: ⁵D₀ → ⁷F₂ transition can be linearly related to the temperature. The highest sensitivity of 0.46% K⁻¹ for the present β -NaYF₄:Ce³⁺/Tb³⁺/Eu³⁺ phosphor make it a promising candidate for temperature sensing.

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Figure captions

Fig. 1 XRD patterns of the as-synthesized NaYF₄ (a), NaYF₄:Ce³⁺ (b), NaYF₄:Ce³⁺/Tb³⁺ (c) and NaYF₄:Ce³⁺/Tb³⁺/Eu³⁺ samples.

Fig. 2 (a) Low magnification, (b) high magnification and (c, d) typical individual FE-SEM images, (e) EDS spectrum (the Si peaks arising from measurement) and morphology sketch for the as-synthesized β -NaYF₄:10%Ce³⁺, 30%Tb³⁺, 1%Eu³⁺ sample.

Fig. 3 Excitation spectra, emission spectra of β -NaYF₄:10%Ce³⁺ (a), β -NaYF₄:10%Ce³⁺, 30%Tb³⁺ (c) and β -NaYF₄:10%Ce³⁺, 30%Tb³⁺, 10%Eu³⁺ (e); Schematic diagram of energy transfer process in the corresponding Ce³⁺, Tb³⁺ and Eu³⁺ doped β -NaYF₄ samples (b, d and f).

Fig. 4 Emission spectra ($\lambda_{\text{ex}} = 248 \text{ nm}$) and the corresponding luminescent photographs of β -NaYF₄:10%Ce³⁺, x%Tb³⁺ samples with different Tb³⁺ dopant concentrations from 0 mol% to 50 mol%. Insets are the energy transfer efficiency $\eta_{\text{Ce-Tb}}$ and Tb³⁺ emission intensity in the as-synthesized samples as a function of Tb³⁺ concentration, respectively.

Fig. 5 Emission spectra ($\lambda_{\text{ex}} = 248 \text{ nm}$) of β -NaYF₄:10%Ce³⁺, 30%Tb³⁺, y%Eu³⁺ samples with different Eu³⁺ dopant concentrations from 0 mol% to 20 mol%. Insets are the energy transfer efficiency $\eta_{\text{Tb-Eu}}$ and Eu³⁺ emission intensity in the as-synthesized samples as a function of Eu³⁺ concentration, respectively.

Fig. 6 (a) PL decay curves of Tb³⁺ ions (⁵D₄ → ⁷F₅) in β -NaYF₄:10%Ce³⁺, 30%Tb³⁺, y%Eu³⁺ samples. All the decay spectra were recorded by monitoring the emission at 542 nm under an excitation of 248 nm; (b) Dependence of the decay time of Tb³⁺ ions

on the Eu^{3+} dopant concentration; (c) PL decay curves of Eu^{3+} ions ($^5\text{D}_0 \rightarrow ^7\text{F}_2$) in $\beta\text{-NaYF}_4\text{:10\%Ce}^{3+}, 30\%\text{Tb}^{3+}, y\%\text{Eu}^{3+}$ samples. All the decay spectra were recorded by monitoring the emission at 614 nm under an excitation of 248 nm; (d) Dependence of the decay time of Eu^{3+} ions on the Eu^{3+} dopant concentration.

Fig. 7 CIE chromaticity diagrams of $\beta\text{-NaYF}_4\text{:10\%Ce}^{3+}, 30\%\text{Tb}^{3+}, y\%\text{Eu}^{3+}$ ($y = 0 \sim 20$) phosphors. Insets are the luminescent photographs of the corresponding samples under a 254 nm UV lamp.

Fig. 8 Energy level mode for the energy transfer processes of $\text{Ce}^{3+} \rightarrow \text{Tb}^{3+} \rightarrow \text{Eu}^{3+}$ in the $\beta\text{-NaYF}_4$ host. P1: excitation into the 4f-5d transition of Ce^{3+} ion; P2: transfer of the excitation energy to Tb^{3+} ion; P3: energy migration among the Tb^{3+} ions; P4: trapping of the migrating energy by Eu^{3+} ion; P5: Cross-relaxation process between the $^5\text{D}_3$ level of Tb^{3+} ion and $^7\text{F}_0$ level of Eu^{3+} ion; P6: emission from Eu^{3+} ions; P7: competitive emission from Tb^{3+} ion; P8: emission from Ce^{3+} ion.

Fig. 9 (a) Temperature-dependent luminescence of $\beta\text{-NaYF}_4\text{:10\%Ce}^{3+}, 30\%\text{Tb}^{3+}, 0.5\%\text{Eu}^{3+}$ sample under the excitation of 248 nm ultraviolet light; (b) The normalized emission spectra of $\beta\text{-NaYF}_4\text{:10\%Ce}^{3+}, 30\%\text{Tb}^{3+}, 0.5\%\text{Eu}^{3+}$ sample in the wavelength region of 520-640 nm; (c) Dependence of FIR ($I_{\text{Eu}}/I_{\text{Tb}}$) on temperature (300 ~ 573 K) for Ce^{3+} , Tb^{3+} and Eu^{3+} co-doped $\beta\text{-NaYF}_4$ sample. The fitted line for the experimental data is also provided in (c).