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Hydrothermal syntheses, luminescent properties, and temperature sensing of monodisperse Tb-doped NaCeF₄ nanocrystals†

Haoran Qin,^{ab} Xinghong Gong,^{ID} a Zundu Luo^a and Yidong Huang^{ID} *a

Monodisperse Tb-doped NaCeF₄ nanocrystals were synthesized *via* a hydrothermal method. The morphology, and room temperature and temperature dependent luminescent properties were investigated. Excited at 254 nm, the emissions of Ce³⁺ at 270–370 nm and those of Tb³⁺ at 475–700 nm can be observed. The strongest visible emission was observed in NaCeF₄:20 at% Tb with a quantum yield of 49%. The efficiency of energy transfer from Ce³⁺ to Tb³⁺ increases with the Tb³⁺ doping concentration and reaches 95% for NaCeF₄:30 at% Tb. The ratio of Tb³⁺ emission to Ce³⁺ emission is sensitive to temperature, and the relative sensitivity was calculated to be 1.0% °C⁻¹ at 60 °C. The mechanisms for this thermal dependence were analyzed in terms of non-radiative relaxation and energy migration.

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Introduction

Lanthanide doped nano-fluorides have gained increasing attention due to their high chemical stability and high resistance to photobleaching.¹ Doped lanthanides give nanocrystals (NCs) unique f–f emission peaks and long fluorescence lifetimes.^{2,3} These properties make lanthanide doped NCs applicable for biological labelling,⁴ displays,^{5,6} solar cells,⁷ *etc.* A nano hexagonal β-NaReF₄ (Re = Y, La–Lu) system as a host for a luminescent temperature probe is mainly due to its good chemical and physical stability and highly efficient up-conversion and downshifting photoluminescence.^{8,9}

Lanthanide ion Ce³⁺ possesses low 4f–5d multiplets and simple 4f multiplets and is widely applied for lanthanide luminescence.^{10,11} Some monodisperse and well-defined NaCeF₄ based NCs have been synthesized. Lei *et al.* synthesized NaCeF₄:Er³⁺/Yb³⁺ NCs *via* the high temperature coprecipitation method.¹² Li *et al.* synthesized NaCeF₄ NCs *via* the liquid–solid-solution hydrothermal method.¹³

Ce³⁺ ions possess broad absorption and emission bands with large cross-sections due to the high oscillator strength of parity allowed 4f–5d transition. The Tb³⁺ ion possesses green emission with a long fluorescence lifetime (millisecond scale), and has been applied for time-resolved photoluminescence imaging.¹⁴ However, the absorption of excitation light by Tb³⁺ is

weak because the corresponding 4f–4f transitions are all parity and spin forbidden. Efficient energy transfer (ET) from Ce³⁺ to Tb³⁺ and bright green emission have been reported in many Ce³⁺ & Tb³⁺ co-doped materials,^{15–18} which inspired researchers to adopt Ce³⁺ and Tb³⁺ combination in nanomaterials. These materials can downshift ultra violet (UV) light to visible light to overcome the poor response of photovoltaic (PV) devices to short wavelength light.^{19,20} Lian *et al.* synthesized NaCeF₄ and NaCeF₄:Tb³⁺ NCs *via* the thermal decomposition method,²¹ and investigated their photoluminescence properties. The NCs synthesized *via* thermal decomposition are monodisperse and highly crystalline.²² However the thermal decomposition method operates at high temperature (about 300 °C).²³ Here we synthesized NaCeF₄:Tb³⁺ NCs by a hydrothermal method.²⁴ With this method, the reaction operates at low temperature (below 200 °C) and monodisperse NCs were successfully synthesized.

Moreover, the 5d–4f emission of Ce³⁺ is sensitive to temperature,²⁵ while the 4f–4f emission of Tb³⁺ is not, which may be because the 4f multiplets are shielded by outer 5s and 5p multiplets.²⁶ With the different responses to temperature between Ce³⁺ and Tb³⁺, their fluorescence intensity ratio (FIR) may act as a probe for temperature sensing. Some Ce³⁺ & Tb³⁺ co-doped phosphors have been investigated.^{27–29} However, investigations on Ce³⁺ and Tb³⁺ induced FIR temperature sensing in NCs are rare.

In this article, we synthesized NaCeF₄:Tb³⁺ NCs by a hydrothermal method. The morphology and structure of NaCeF₄:Tb NCs were investigated. Furthermore, room temperature (RT) and temperature dependent luminescent properties of NaCeF₄:Tb NCs were studied. The materials are monodispersed and exhibit bright emission and a high quantum yield, and may

^aKey Laboratory of Optoelectronic Materials Chemistry and Physics, Fujian Institute of Research on the Structure of Matter, Chinese Academy of Sciences, Fuzhou, Fujian 350002, China. E-mail: huyd@fjirsm.ac.cn

^bUniversity of Chinese Academy of Sciences, Beijing 100039, China

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have potential application for enhancing the energy conversion efficiency of PV devices. Moreover, since the FIR between Ce^{3+} and Tb^{3+} emission correlates strongly with temperature, $NaCeF_4:Tb$ NCs may have potential application in FIR nanothermometers.

Experimental

Materials

$Ce(NO_3)_3 \cdot 6H_2O$, $Tb(NO_3)_3 \cdot 5H_2O$, oleic acid (OA), sodium hydroxide, ammonium fluoride, and cyclohexane were purchased from the Aladdin Chemical Reagent Company. Ethanol was purchased from the Sinopharm Chemical Reagent Company. All the chemicals were of analytical grade and used without further purification. Deionized water was used throughout the experiments.

Synthesis

Typically, for synthesis of $NaCeF_4$ NCs, 1.5 ml H_2O , 0.6 g sodium hydroxide, 20 ml OA, and 10 ml ethanol were mixed. Then 0.5 mmol $Ce(NO_3)_3$ (0.5 M) aqueous solution was added into the above solution. Lastly, 3 mmol ammonium fluoride aqueous solution (2 M) was added into the mixed solution. After stirring for 30 min, the colloidal solution was transferred into a 50 ml Teflon-lined autoclave and was heated at selected $170^\circ C$ for 6 h. The systems were then cooled down to room temperature. The final products were collected by centrifugation, washed with ethanol, and then dispersed in cyclohexane. The doping of Tb^{3+} was conducted by adding $Tb(NO_3)_3$ with designed concentrations to the reaction system.

Characterization

X-ray diffraction (XRD) analysis was carried out on a Rigaku-Dmax 2500 diffractometer using $Cu-K\alpha$ radiation ($\lambda = 0.154$ nm). The size and morphology of the samples were observed using a transmission electron microscope (TEM) JEOL-2010 equipped with an energy dispersive X-ray spectrometer (EDS). Fourier-transform infrared (FTIR) spectra were recorded in KBr discs using a Magna 750 FTIR spectrometer. The temperature dependent and RT emission, RT excitation spectra, quantum yield, and RT fluorescence decay curves were recorded from pressed tablets of the $NaCeF_4:Tb$ NCs powder using an FLS 980, Edinburgh.

Results and discussion

Components and morphology

The XRD patterns of $NaCeF_4$ NCs with different Tb^{3+} doping concentrations match well with those of $\beta-NaCeF_4$ (pdf#50-0154) (ESI Fig. S1[†]). No additional phases were found even in the sample with 30 at% Tb^{3+} doping, indicating that Tb^{3+} has been efficiently incorporated into the host of $\beta-NaCeF_4$. The EDS pattern of $NaCeF_4:20$ at% Tb is shown in ESI Fig. S2[†]. The results of XRD and EDS analyses reveal high purity of the as-prepared samples. OA was chosen as the capping agent to control the growth of NCs and make NCs non-polar solvent

soluble. The as-prepared NCs can be well dispersed in cyclohexane and the solution is transparent (ESI Fig. S3(a)[†]). The presence of OA capping on the surface of the $NaCeF_4$ NCs was verified from the FTIR spectrum (ESI Fig. S3(b)[†]).

The TEM pattern of $NaCeF_4:20$ at% Tb NCs is shown in Fig. 1. The shape and size of the as-prepared NCs can be seen in Fig. 1(a–c); the NCs are a hexagonal prism and monodisperse. The length of NCs is parallel to the hexad axis, and hence the crystal growth direction is [001]. The length of $NaCeF_4:20$ at% Tb NCs has been estimated by randomly analysing 200 NCs. The mean length of the NCs is 170 nm and the distribution frequency of the lengths can be seen in Fig. 1(d), which shows good uniformity of the NCs. The cross-section diameters of the NCs are about 45 nm. The aspect ratio of the NCs was therefore calculated to be 3.8. From the high resolution TEM (HRTEM) image of the NC pattern shown in Fig. 1(e), clear lattice fringes can be observed, which indicate good crystallinity. Fig. 1(f) shows the Fourier transform image of the square area in

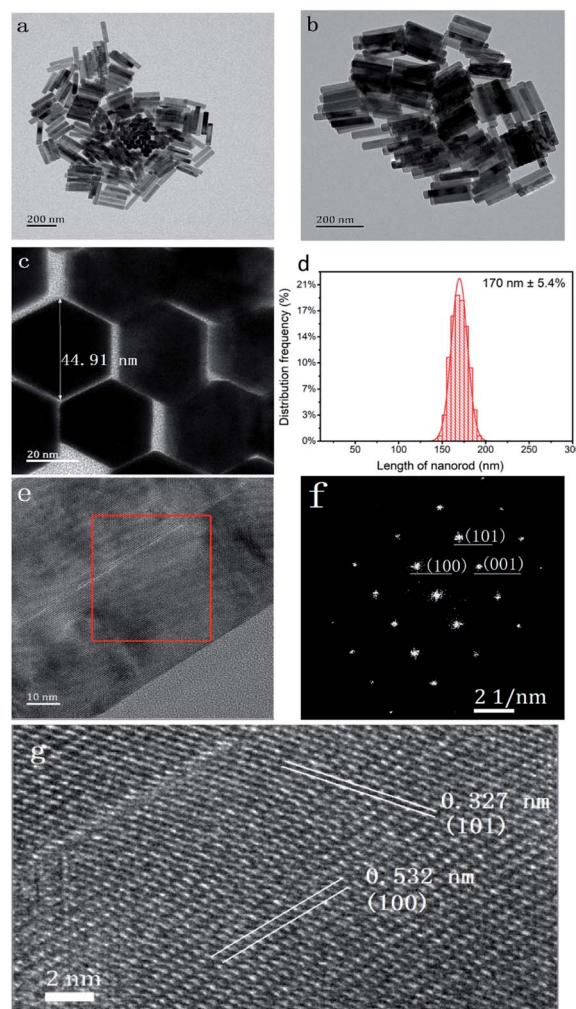


Fig. 1 (a and b) TEM images of $NaCeF_4:20$ at% Tb NCs. (c) HRTEM image of the NCs. (d) Distribution frequency of the lengths of the NCs. (e) HRTEM image of the NCs. (f) Fourier transform image of the square area in (e). (g) Zoom in of the square area in (e) with the labelled interplanar spacing.



Fig. 1(e). In Fig. 1(g), two interplanar distances were labelled 0.532 and 0.327 nm, which are in accordance with the (100) and (101) interplanar distances of NaCeF₄,³⁰ respectively.

Luminescent properties

The excitation spectra of the NaCeF₄:Tb NCs are similar, and the excitation spectrum of the NaCeF₄:20 at% Tb monitoring emission at 543 nm is shown in Fig. 2. There are two types of excitation signals in Fig. 2. The broad and strong band originates mainly from the parity-allowed 4f–5d transitions of Ce³⁺, and the narrow and weak peaks come from the parity-forbidden 4f–4f transitions from the ground state to the corresponding excited multiplets of Tb³⁺. The strong band is centered at 256 nm and matches well with a commercial low-pressure mercury lamp with a central wavelength of 254 nm. Under excitation of the lamp, the cyclohexane solution with NaCeF₄:20 at% Tb NCs dispersed emits bright green fluorescence (ESI Fig. S4†). Under excitation at 254 nm, the emission spectra of the NaCeF₄ NCs with different Tb doping concentrations are shown in Fig. 3(a). The emission spectra for different samples were measured under the same conditions. The broad emission bands around 305 nm originate from the 5d–4f transition of Ce³⁺. The emission peaks centered at 489, 543, 584, and 620 nm are the 4f–4f transitions from ⁵D₄ to ⁷F_{6,5,4,3} multiplets of Tb³⁺, respectively. Fig. 3(b) shows the changes of fluorescence intensities at 305 and 543 nm with the Tb doping concentration. Fluorescence intensity at 305 nm decreases with the increase of the Tb concentration, which indicates the existence of the ET process from Ce³⁺ to Tb³⁺. The Ce³⁺ emission ranges from 275 to 360 nm, which overlaps with some excited levels of Tb³⁺ (ESI Fig. S5†). Hence the ET from Ce³⁺ to Tb³⁺ is resonant. The ET efficiency can be expressed by the following equation:³¹

$$\eta_T = 1 - \frac{I_S}{I_{S0}}$$

where I_S and I_{S0} are the integrated fluorescence intensities (270–370 nm) of Ce³⁺ with and without Tb³⁺ doping, respectively. The ET efficiency for the NaCeF₄:xat% Tb NCs ($x = 1, 3, 5, 10, 15, 20, 25, 30$) was therefore calculated to be 10%, 16%, 45%, 63%, 71%, 78%, 88%, and 95%, respectively. In Fig. 3, the sample with 20 at% Tb doping shows the strongest visible emission and the visible quantum yield was measured to be 49%. With the Tb

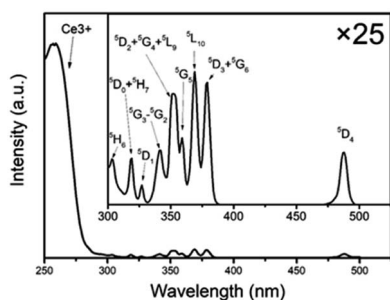


Fig. 2 Excitation spectrum of NaCeF₄:20 at% Tb NCs monitoring at Tb³⁺ ⁵D₄ → ⁷F₅ transition ($\lambda_{em} = 543$ nm). The inset spectrum is intensity magnified 25 times the one in the range from 300 to 550 nm.

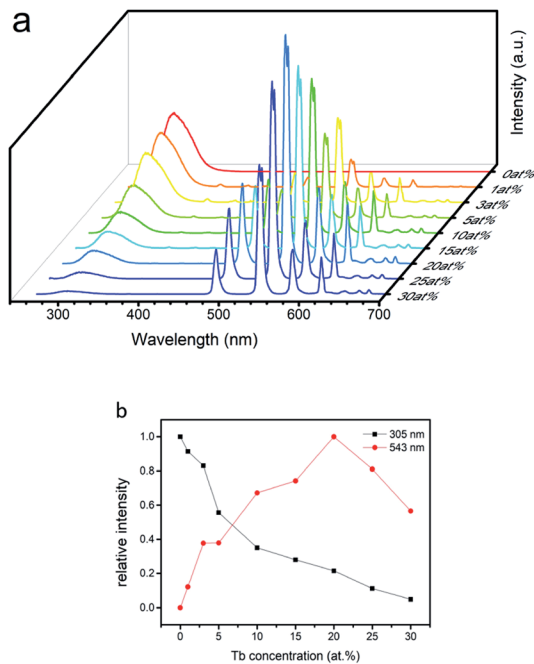


Fig. 3 (a) Emission spectra of NaCeF₄:Tb NCs under excitation at 254 nm. (b) Fluorescence intensity at 305 and 543 nm versus the Tb concentration.

doping concentration being increased further, the intensity of Tb emission decreases, which indicates the presence of concentration dependent fluorescence quenching in the NCs.

Fluorescence decay curves at 543 nm for NaCeF₄ NCs with different Tb doping concentrations were measured under excitation at 254 nm. The results on a semilog coordinate are depicted in Fig. 4. Obviously, the curves exhibit simple exponential decay behaviour and can be expressed by

$$I = I_0 \exp(-t/\tau)$$

where I is the fluorescence intensity at time t , I_0 is the fluorescence intensity at $t = 0$, and τ is the fluorescence lifetime of the excited multiplet ⁵D₄. With the Tb concentration being increased from 1 at% to 30 at%, the fluorescence lifetime

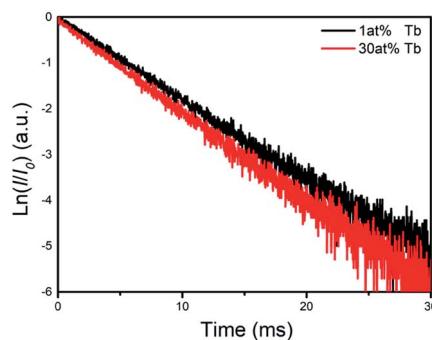


Fig. 4 Semi-logarithmic coordinates of the fluorescence decay curves of Tb³⁺ ⁵D₄ → ⁷F₅ transition ($\lambda_{em} = 543$ nm) under excitation at 254 nm for the sample with different Tb doping concentrations.



decreases from 5.59 to 4.97 ms. The fluorescence lifetime maintains at the millisecond level for high Tb doping concentrations.

Temperature sensing behaviour

NaCeF₄:5 at% Tb NCs exhibit high and similar Ce and Tb emission intensities, which are suitable for temperature sensing.³² The temperature dependent fluorescence spectra of NaCeF₄:5 at% Tb NCs under excitation at 254 nm are shown in Fig. 5(a). The trends of the temperature dependent emission intensity of Ce³⁺ and Tb³⁺ are different. I_{Ce} is defined as the integrated Ce³⁺ emission intensity in the range of 270–370 nm. I_{Tb} and $I_{Tb\ green}$ are defined as the integrated Tb³⁺ emission intensities in the ranges of 475–700 nm and 525–570 nm, respectively. As shown in Fig. 5(b), when the temperature is below 0 °C, I_{Ce} remains unchanged (100% ± 2%); when the temperature is higher than 0 °C, I_{Ce} decreases with temperature rise and to 83% at 60 °C. However, both I_{Tb} and $I_{Tb\ green}$ increase with the temperature to about 150% at 60 °C. Based on the Ce³⁺ configuration coordinate diagram shown in Fig. 6, the trend of temperature dependent I_{Ce} can be partially explained. The nonradiative transition (process A) needs assistance of phonons to pass through an energy barrier ΔE to the 4f ground states,³³ and hence increasing the temperature will promote this non-radiative transition³⁴ and decrease the overall quantum efficiency. The temperature dependent luminescence spectra of NaCeF₄ NCs can be seen in ESI Fig. S6.† ΔE was calculated to be 0.41 eV according to the Arrhenius formula. For materials with a high Ce³⁺ concentration, there is another temperature quenching mechanism: thermally activated concentration quenching.³⁵ This mechanism depends on the thermally enhanced nonradiative energy migration among Ce³⁺ and then transfer to defects.³⁶ For Tb³⁺ and Ce³⁺ co-doped materials, the defects could also be Tb³⁺. Hence, Tb³⁺ emission could be thermally enhanced in materials with a high Ce³⁺

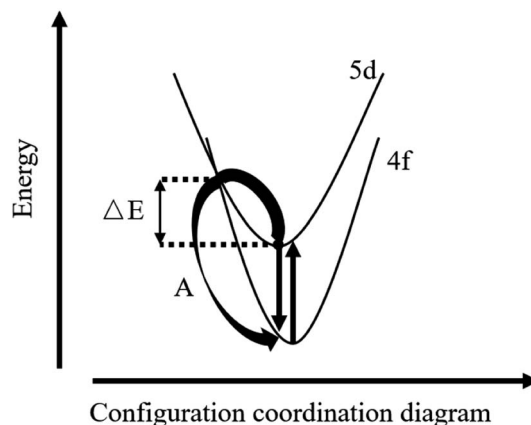


Fig. 6 Ce³⁺ configuration coordinate diagram.

concentration. NaCeF₄:Tb³⁺ possesses a high Ce³⁺ concentration, and hence temperature sensitivity may be higher than those with a low Ce³⁺ concentration.

As illustrated in Fig. 7(a and b), both the FIRs I_{Tb}/I_{Ce} and $I_{Tb\ green}/I_{Ce}$ increased monotonously and nonlinearly with temperature. The experimental values in Fig. 7(a and b) can be fitted well with single exponential curves; the relevant expressions are

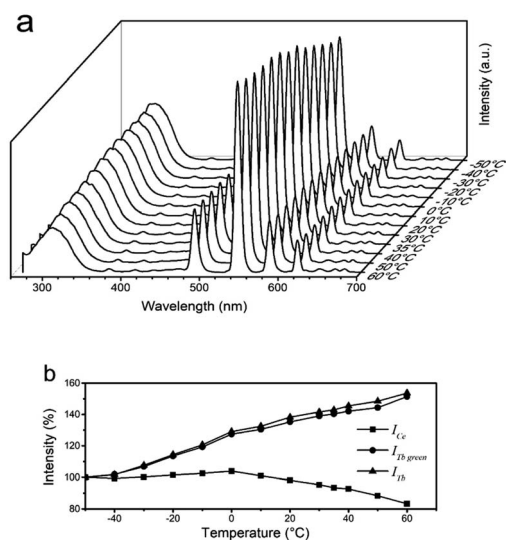


Fig. 5 (a) Temperature dependent luminescence spectra of NaCeF₄:5 at% Tb NCs. (b) Integrated luminescence intensity versus temperature.

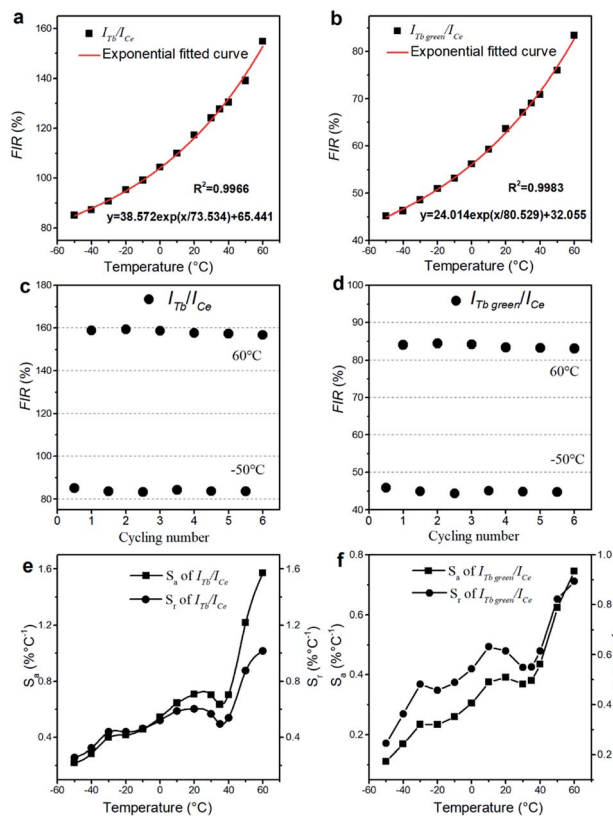


Fig. 7 For NaCeF₄:5 at% Tb NCs. (a and b) Temperature dependent fluorescence intensity ratio with exponential fitted curves (I_{Tb}/I_{Ce} for (a); $I_{Tb\ green}/I_{Ce}$ for (b)). (c and d) I_{Tb}/I_{Ce} and $I_{Tb\ green}/I_{Ce}$ in heating-cooling cycles. (e and f) Temperature dependent absolute sensitivity (S_a) and relative sensitivity (S_r) (I_{Tb}/I_{Ce} for (e); $I_{Tb\ green}/I_{Ce}$ for (f)).



Table 1 Summary of the Ce³⁺ concentration, tendency of the $I_{\text{Ce}}/I_{\text{Tb}}$ ratio with temperature, temperature range and Sr of NaCeF₄:5% Tb and some Ce & Tb thermometers

Ce & Tb activated thermometers	Ce ³⁺ concentration (10 ²⁰ cm ⁻³)	Tendency of the $I_{\text{Ce}}/I_{\text{Tb}}$ ratio with temperature	Temperature range (°C)	Sr (% °C ⁻¹)	Ref.
YBO ₃ :1% Ce,1% Tb	1.8	Linear	15–55	0.498	37
β-NaYF ₄ :10% Ce,5% Tb	12.2	Linear	30–290	0.65	38
LaOBr: 1% Ce,3% Tb	1.6	Linear	20–160	0.42	27
K ₂ BaCa(PO ₄) ₂ :3% Ce,3% Tb	3.0	Linear	20–200	0.35	39
Sr _{30.6} Ce(PO ₄) ₃ :40% Tb	22.7	Linear	25–300	0.384	40
BaY ₂ Si ₃ O ₁₀ :2% Ce,18% Tb	1.9	Linear	20–260	0.30	41
NaCeF ₄ :5% Tb	112.6	Nonlinear	–50 to 60	1.0	This work

shown as insets in Fig. 7(a and b), respectively. Repeatability and stability are important for practical application of thermometers. Six cycles of heating–cooling experiments were thus conducted, and the results are shown in Fig. 7(c and d). The results indicate that $I_{\text{Tb}}/I_{\text{Ce}}$ and $I_{\text{Tb green}}/I_{\text{Ce}}$ are reversible and stable. The absolute and relative sensitivity (S_a , S_r) can be expressed as⁴²

$$S_a = \left| \frac{d\text{FIR}}{dT} \right|$$

$$S_r = \left| \frac{1}{\text{FIR}} \times \frac{d\text{FIR}}{dT} \right|$$

where T is the temperature. The calculated S_a and S_r versus temperature were plotted in Fig. 7(e and f). The values of S_r for $I_{\text{Tb}}/I_{\text{Ce}}$ and $I_{\text{Tb green}}/I_{\text{Ce}}$ below 40 °C are similar. When the temperature exceeds 40 °C, the S_r of $I_{\text{Tb}}/I_{\text{Ce}}$ is larger than that of $I_{\text{Tb green}}/I_{\text{Ce}}$. The maximum S_r of $I_{\text{Tb}}/I_{\text{Ce}}$ and $I_{\text{Tb green}}/I_{\text{Ce}}$ reaches 1.0% °C⁻¹ and 0.9% °C⁻¹ at 60 °C, respectively, and the values may be higher at a higher temperature. In Table 1, compared with others, the tendency of the $I_{\text{Ce}}/I_{\text{Tb}}$ ratio with temperature for NaCeF₄:5% Tb is unique and NaCeF₄:5% Tb has the highest Sr, which may be ascribed to its highest Ce³⁺ concentration. The high temperature sensitivity and high stability indicate that this NC could be a candidate for use as a UV-excited luminescence ratio metric nanothermometer.

Conclusion

Monodisperse Tb doped NaCeF₄ NCs with high crystallinity and high uniformity have been prepared *via* a hydrothermal method. Under excitation at 254 nm, the NCs exhibit UV emission of Ce³⁺ and characteristic visible emission of Tb³⁺. Fluorescence spectra show the existence of ET from Ce³⁺ to Tb³⁺, and NaCeF₄:20 at% Tb displays the strongest visible emission with a quantum yield of 49%. The temperature dependent fluorescence spectra of NaCeF₄:5 at% Tb indicate that the ratio of Tb emission to Ce emission increases monotonously with temperature. Compared with other Ce & Tb thermometers, the Tb doped NaCeF₄ NCs have higher maximum S_r , which may be ascribed to the high Ce³⁺ concentration in the NCs. Due to the uniform nanomorphology, unique luminescent properties and high temperature sensitivity, the Tb doped

NaCeF₄ NCs may have applications in PV devices and FIR nanothermometers.

Conflicts of interest

There are no conflicts to declare.

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