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Temperature sensing performance based on up-conversion luminescence in hydrothermally synthesized Yb³⁺, Er³⁺ co-doped NaScF₄ phosphors

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NaScF₄:Yb³⁺, Er³⁺ crystals were successfully hydrothermally synthesized using distilled water as a single solvent. The phase and morphology were characterized by XRD and SEM. Compared with organic solvents such as ethanol, ethylene glycol and ether, the molar ratio of Na/F/Sc plays an important role in the synthesis process of NaScF₄ crystal. Morphological control was achieved by changing the types of additives, and the relationship between morphology and luminescence properties was explored. The NaScF₄: Yb³⁺, Er³⁺ phosphors exhibit strong green and red UC emissions under the excitation of 980 nm NIR. Optimal concentrations of Yb³⁺ and Er³⁺ for up-conversion luminescence performance were identified as 10% and 2%, respectively. Without any subsequent heat treatment process, the obtained NaScF₄:10%Yb³⁺, 2%Er³⁺ showed good temperature sensitivity. The temperature sensing ability was investigated by employing the dependence of fluorescence intensity ratio (*FIR*) of the two thermal coupling energy levels of Er³⁺ (²H_{11/2}→⁴|_{15/2} and ⁴S_{3/2}→4|_{15/2}) on temperature; the maximum sensitivity *S_A/S_R* was 0.00256 K⁻¹/0.00317 K⁻¹ at 548 K, and it increased to 0.00328 K⁻¹/0.00413 K⁻¹ after adding EDTA. In addition, the evaluation of temperature uncertainty during temperature measurement was performed, which were 0.073 K and 0.095 K in the presence and absence of EDTA, respectively. Compared with some other reported materials, the obtained material shows a relatively superior temperature sensitivity, which provides new ideas for the improvement of temperature-sensitive materials.

Introduction

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A series of materials can be produced by doping rare earth ions into different substrates, such as optical materials, permanent magnetic materials, hydrogen storage materials, catalytic materials, ceramic materials, superconducting materials, etc.1-3 Rare earth (RE) is known as the "vitamin of modern industry" and "treasure house of new materials in the 21st century", and it's recognized as an important strategic resource globally.4-7 At present, RE elements have been widely used in many fields, such as petrochemical industry, metallurgy, energy sources, environmental protection, agriculture and so on.8-10 Of course, they have catched the eyes of numerous researchers by virtue of their unique physicochemical properties. Researchers have investigated multifarious inorganic materials, including silicates, carbonates, aluminates, phosphates, molybdate, nitrides, fluoride and the like.11-21 RE-based fluoride materials have attracted much attention due to their mild synthesis conditions, favorable

research on fluorides has covered many systems from simple to complex. RE-based fluorides represent a promising fluorescent host matrix, especially the Sc3+-based fluorides, that's mainly because Sc3+ has a unique atomic electron configuration and a smallest ionic radius compared to other RE³⁺ ions.²⁷⁻²⁸ And that's why much effort has been put into NaScF₄ recently.²⁹⁻³² Chen's group studied the crystal structure, spectral properties and application of NaScF₄ in biological detection.²⁹ Yang and co-workers studied the preparation of NaScF₄ microcrystals, solid phase nuclear magnetic resonance and up-conversion luminescence.³⁰ Cao and co-workers have successfully synthesized a series of Ln³⁺-doped NaScF₄ crystals with various phase and morphology.³¹ Zhang and co-workers reported that Yb³⁺, Er³⁺ co-doped NaScF₄ nanophosphors from green to red UC emissions can be realized by adjusting the reaction time.³² All in all, the research on NaScF₄:Ln³⁺ has been relatively comprehensive, connecting to energy transfer, up conversion luminescence, and down morphological characteristics and different preparation methods. However, NaScF₄ as a matrix for temperature sensing material have largely been neglected before; the existing rich reports cannot mean the investigation come to an end in this area, on the contrary, they provide more comprehensive information basis for further research.

chemical stability and excellent optical properties,²²⁻²⁶ and the

In this paper, $NaScF_4$: Ln^{3+} phosphors were synthesized using distilled water as a single solvent. On the basis of the synthesis

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of pure NaScF₄ host, the up-conversion luminescence properties and the mechanism of Yb3+ and Er3+ ions co-doped NaScF₄ phosphors were studied and their optimal doping concentration was gained through the control variable method as well as fluorescence intensity analysis. Afterwards, the relationship between the morphology and luminescence properties of NaScF₄:10%Yb³⁺, 2%Er³⁺ phosphors with different surfactants was also investigated, which provided a basis for the subsequent research. Finally, the temperature sensitivity of NaScF4: 10%Yb3+, 2%Er3+ phosphors in the presence and absence of EDTA was studied in detail for the first time. For all we know, the synthesis of temperature sensitive materials usually adopt high temperature solid state method or other methods followed by treatment of high temperature calcination.³³ The temperature sensitivity characteristics of hydrothermal synthetic materials without a follow-up hightemperature treatment steps were studied in our work, and the effects of EDTA on temperature sensitivity was analyzed. The conclusions of this work were then compared with some other reported literatures to analyze the advantages of the obtained material.

Experimental section

Chemicals

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As the starting materials, the rare earth oxides RE_2O_3 (99.99%, Ln = Sc, Yb and Er) were purchased from Ganzhou Guangli High-tech materials Company (China), NH₄F (99.9%), NaCl (99.9%), ethylene diamine tetraacetic acid (EDTA), citric acid, sodium dodecylbenzenesulfonate (SDBS) and hydrochloric acid (HCl) were purchased from Aladdin. All chemicals were analytical reagents, and used directly for products synthesis without further refinement. The solutions of rare-earth chloride including ScCl₃, YbCl₃ and ErCl₃ were obtained by dissolving a calculated amount of rare earth oxide in hydrochloric acid under conditions of heating and stirring constantly, and then driving away the needless hydrochloric acid by evaporation.

Synthesis

 $NaScF_4$ crystal and Ln^{3+} (Ln = Yb and Er) co-doped $NaScF_4$ crystals were prepared by a general and mild hydrothermal method. Here, the synthesis of NaScF₄:10%Yb³⁺, 2%Er³⁺ is used as an example. In a typical synthesis process, 30 mL of deionized water, 0.88 mmol ScCl₃ (1 M, 880 μ L), 0.1 mmol YbCl3 (1 M, 100 $\mu\text{L}),$ 0.02 mmol ErCl3 (1 M, 20 $\mu\text{L})$ were mixed together under stirring for a quarter, then 0.527 g NaCl was added into the above mixed solution, after stirring for half an hour, 4 mmol NH₄F solution was added followed by stirring for another 30 minutes, and the obtained mixture was then poured into 50 mL Teflon reaction kettle held in a stainlesssteel autoclave, sealed and heated at 200 °C for 24 h. After reaction finished, collected the products until it's cooled to room temperature naturally, and then washed several times with deionized water and ethanol to remove any possible ionic remnant impurities and dried at 60 °C for 12 h. Meanwhile,

other samples were also synthesized using the same method expect different types and concentrations: of the loged the ions; in addition, if surfactants were used, added them firstly.

Characterization

Phase purities identification of the samples was carried out by powder X-ray diffraction (XRD) performed on a Purkinje General Instrument MSALXD3 using Cu K α radiation (λ = 0.15406 nm) produced at 20 mA, 36 kV, and at a scanning rate of 8° min⁻¹ in the 2 θ range from 10° to 60°. The morphology analysis of the samples was investigated by a field emission scanning electron microscopy (FE-SEM, Hitachi, S-4800) with an accelerating voltage of 10 kV. The UC emission spectra were obtained by using a LS-55 spectrometer (PerkinElmer) from 450 to 750 nm with a 980-nm NIR continuous wave (CW) laser diode (LD) coupled to a fiber as the excitation source. The sample was heated from 298 K to 573 K by using the high temperature fluorescence controller (TAP-02) to measure the curve of up-conversion luminescence intensity changed with temperature. Up-conversion measurements were performed in a stable environment of 25 °C, and the rest were performed at room temperature.

Results and discussion

3.1. Phase and morphology

3.1.1. Pure NaScF₄ host and NaScF₄:10%Yb³⁺,2%Er³⁺ phosphors



Fig. 1 (a) XRD patterns of pure NaScF₄ and NaScF₄:10%Yb³⁺, 2%Er³⁺ phosphors, (b) SEM image of NaScF₄ and (c) SEM image of NaScF₄:10%Yb³⁺, 2%Er³⁺.

Fig. 1a shows the XRD patterns of NaScF₄ and NaScF₄:10%Yb³⁺, 2%Er³⁺ samples, which were prepared under molar ratio of Na:F:RE = 9:4:1. There are no miscellaneous peaks at all compared with the standard card (JCPDS no.20-1152), which

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indicates that NaScF4 and NaScF4:10%Yb³⁺, 2%Er³⁺ are both attributed to pure hexagonal phase with an unit cell parameters of a = b = 12.97 Å, c = 9.27 Å and z = 18. In addition, the characteristic diffraction peak corresponding to the (221) crystal plane has a slight shift toward the low 2 θ direction after doping the two ions of Yb³⁺ and Er³⁺ (magnified in Fig. 1a), which reveals that Yb³⁺ and Er³⁺ ions have been successfully incorporated into the crystal lattice of NaScF4 crystals and occupied the position of the original Sc^{3+} ions. The ionic radius of Yb³⁺ and Er³⁺ is larger than that of Sc³⁺, and when the Sc³⁺ ions are replaced by Yb3+ and Er3+, the unit cell volume becomes larger, which is visually expressed as the diffraction peak shifts to a lower 2 θ degree.³⁴ It is also observed that the intensity of the diffraction peak is significantly increased when Sc3+ is replaced by Yb3+ and Er3+, which is a manifestation of increased crystallinity.



Fig. 2 XRD patterns of pure NaScF $_4$ host with different Na/Sc (a) and F/Sc (b) ratios, respectively.

Fig. 1b and c show the high magnification SEM photograph of NaScF₄ and NaScF₄:10%Yb³⁺,2%Er³⁺, respectively. By comparing the SEM images of the two samples, it can be easily found that the size of the sample after doping has changed greatly from an average of 4 μ m to an average of 10 μ m, which is consistent with the result reflected by the XRD patterns for better crystallinity in Figure 1a. As the crystal size changes, the morphology changes from a cubic block (Fig. 1b) to Action action and the star shape (Fig. 1c). Action action at the star shape (Fig. 1c). Action at the star shape (Fig. 1c). Action at the star and amount of doped rare earth ions have a significant effect on the size and morphology of the host material, ^{31,35} so the huge difference in crystal morphology here should be attributed to the doping of Yb³⁺ and Er³⁺ ions. Due to their effect on crystal growth, the doped Yb³⁺ and Er³⁺ ions cause the growth rate of diverse crystal planes of the crystal different, which naturally manifests as the difference in morphology. Specifically, the doped ions are adsorbed on certain crystal planes to increase their growth rate, such as (111) and (221), and the crystals grow relatively rapidly along these crystal planes. However, there's no such driving force when undoped, which reasonably explains the reason for the different morphologies in Figure 1 b and c.³⁶

3.1.2. The Na/F/Sc ratio

The preparation process of NaScF₄ matrix can be affected by many factors, and the influence of raw material ratio is mainly explored here. The results are shown in Fig. 2, which is the XRD patterns of pure NaScF₄ host prepared with different Na/F/Sc ratios. First of all, the optimal Na/Sc molar ratio required for the synthesis was explored by a control variable method. As shown in Fig. 2a, the XRD pattern changes regularly with increase of Na/Sc ratio, and the sample remains in the mixed phase of monoclinic ScF₃ (JCPDS no.46-1243) and hexagonal NaScF₄ (JCPDS no.20-1152) until the ratio equal to 8. Within the scope of the experimental study, the prepared samples are always pure and belong to the hexagonal NaScF₄ phase as the Na/Sc ratio continues to increase to 9. As reported that the power to form NaScF₄ is stronger than that of ScF₃ in the original mixture of reagents and increasing the concentration of Na⁺ is beneficial to the production of NaScF₄.³⁷ However, it is learned from the literature that the Na/Sc required to synthesize pure NaScF₄ under organic solvent conditions is much lower, ³¹ so it can be audaciously that the quantity of Na⁺ and organic solvents such as ethylene glycol both provide positive driving force for the formation of NaScF4 and they work synergistically. If the organic solvents were replaced by distilled water, the Na⁺ ions need to show a greater boost so that its concentration needs to be increased to a higher level.³⁷ As a result, the four peaks corresponding to the (100), (200), (210) and (211) crystal planes of ScF₃ (JCPDS 46-1243) disappear gradually. That's the reason why the Na/Sc ratio is much higher than that when organic solvents are used.

Next, the most appropriate F/Sc ratio for the synthesis of NaScF₄ was probed in the same way. As indicated in Fig. 2b, with the molar ratio of F/Sc from 3 to 4, the phase transformation from monoclinic ScF₃ to hexagonal NaScF₄ can be observed, which is basically consistent with the conclusion obtained by using organic solvents,³¹ and prove that the effect of F⁻ ions on the final crystal type formed in the mixed solution depends on its own concentration not the solvent. The replacement of the solvent only affects the diffusion of F⁻ ions and thus the rate of nucleation, which results in different sizes of crystal particles rather than different phases of crystal particles.³⁸ Finally, in accordance with the principle of

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experimental facts, the most suitable Na/F/Sc ratio is 9:4:1 in our work and the subsequent sample synthesis is based on this.

3.1.3. Morphology of $\mathsf{NaScF}_4{:}10\%Yb^{3+},\ 2\%Er^{3+}$ under different surfactants



Fig. 3 XRD patterns (a) and SEM images of NaScF₄:10%Yb³⁺, 2%Er³⁺ using different surfactants: (b) EDTA, (c) SDBS and (d) Citric Acid; schematic diagram of the evolution of crystal morphology (e).

To obtain a product with uniform appearance and excellent UC luminescent properties, three kinds of surfactants were added severally during the synthesis of NaScF₄:10%Yb³⁺, 2%Er³⁺ phosphors under the premise that other conditions being equal, and the typical XRD patterns and SEM images of the products are given in Fig. 3. It can be observed that all the XRD patterns of the NaScF₄: 10%Yb³⁺, 2%Er³⁺ phosphors prepared using three different additives are perfectly matched with the standard card (JCPDS no. 20-1152) and reflects the increasing crystallinity from citric acid to EDTA. Also, there is a huge difference in the morphology among them: a short rod shape under EDTA condition (Fig. 3b), approximately uniform granularity under SDBS condition (Fig. 3c) and a relatively serious agglomeration under citric acid condition (Fig. 3d). Fig. 3e simply reveals the evolution of the NaScF₄:10%Yb³⁺, 2%Er³⁺ crystals morphology under conditions of different surfactants, which is a straightforward reflection of the changes described above. The relative intensity of the diffraction peaks corresponding to the (221) and (224) crystal planes of the crystals under EDTA condition is significantly enhanced (marking with blue diamond in Fig. 3a),

which means that the crystals preferentially grow along the (221) and (224) crystal planes. The occurrence of these phenomena above is probably due to the diversity in the coupling ability, the complexation mode and its own properties of each surfactant, so there is a selective difference in the crystal face adsorption problem during the reaction, which directly affects the anisotropic growth of the crystal, resulting in variations in morphology and size.^{39, 40}



Fig. 4 UC emission spectra of Yb³⁺, Er^{3+} co-doped NaScF₄ crystals under 980 nm excitation: (a) NaScF₄:x%Yb³⁺, 2%Er³⁺ (x = 4, 6, 8, 10, 12 and 20) and (b) NaScF₄: 10%Yb³⁺, y%Er³⁺ (y = 0.5, 1, 2, 3, 4 and 5), respectively.

3.2. UC luminescence properties and mechanism

A series of experimental studies were carried out to explore the UC luminescence properties of the Yb³⁺, Er³⁺ co-doped NaScF₄ systems. Fig. 4 shows the UC luminescence spectra of NaScF₄:Yb³⁺, Er³⁺ crystals with different doping concentration of Yb³⁺ as well as Er³⁺ ions under 980 nm NIR excitation, which reflects that the optimal doping ratios of Yb³⁺ and Er³⁺ ions are 10% and 2%, respectively (marking with blue diamonds in the figure). Er³⁺ ions have both strong green and red emissions in the NaScF₄ host, and the former (green emission of 515~565 nm) is attributed to the ${}^{2}H_{11/2} \rightarrow {}^{4}I_{15/2}$ and ${}^{4}S_{3/2} \rightarrow {}^{4}I_{15/2}$ energy Published on 11 May 2020. Downloaded on 5/12/2020 2:57:45 AM

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level transitions of Er^{3+} as well as the latter (red emission of 645~680 nm) is derived from the ${}^{4}F_{9/2} \rightarrow {}^{4}I_{15/2}$ energy level transition of Er^{3+} ions.^{38, 41} Besides, since the hexagonal phase NaYF₄ co-doped with Yb³⁺ and Er^{3+} ions are often considered as the most efficient materials for up-conversion of near-infrared light,⁴² we took the NaScF₄:10%Yb³⁺, 2%Er³⁺ as a representative and compared its relative luminous intensity with NaYF₄:10%Yb³⁺, 2%Er³⁺ under 980 nm NIR excitation with the pump power at 0.944 W. The calculation results are that I_{NaScF4}/I_{NaYF4} = 0.965 in the green light region, I_{NaScF4}/I_{NaYF4} = 0.949 in the whole region, respectively (Figure S1).



Fig. 5 (a) The double logarithmic plot of the UC emission intensity varying with pump power for NaScF₄:10%Yb³⁺, 2%Er³⁺, and the inset displays the power dependent UC fluorescence spectra; (b) The fitted slopes for NaScF₄: Yb³⁺, 2%Er³⁺ with different Yb³⁺ concentrations.

Immediately after, the mechanism of up-conversion luminescence of the Yb³⁺/Er³⁺ co-doped NaScF₄ phosphors is studied based on the optimal doping concentration. Fig. 5a shows the double logarithmic variation trend of pump power and the integral intensity which point to the green and red emissions of NaScF₄:10%Yb³⁺, 2%Er³⁺ phosphors, and the inset displays the power dependent UC fluorescence spectra. The dependence of luminescent intensity on power is the key to reveal the mechanism of up-conversion luminescent process of rare earth ions, and the relationship of them can be expressed as:⁴³ DOI: 10.1039/D0DT00809E

 $I \propto P^n$

(1)

The value of n is equal to the number of photons needed to excite the emission level of UC. It's noticeable that the formula above only works in the case of low power density of pump. The integral intensity of UC emission of green and red under different pump power is obtained from the measured experimental data, and the logarithm of the integral intensity as well as power can be calculated, then two slope values of ngreen =1.78 and nred =1.50 are obtained by linear fitting, which suggests that both green and red UC emissions generates from two-photon process.⁴⁵ Furthermore, the slopes for power (P) dependent UC emission intensity (I) were also examined in other samples. Fig. 5b shows the fitted slopes for NaScF₄: Yb³⁺, 2%Er³⁺ with different Yb³⁺ concentrations (from 8% to 20%). Within the range of experimental investigations, as the concentration of Yb3+ increases, the fitted slope values for both green and red emissions show an overall ascend trend. The slope values cover the range of 1.77~2.14 for green emission and 1.50~2.08 for red emission, which again shows that both green and red UC emission should be mainly contributed by the two-photon process.45

Generally speaking, the mechanism of UC luminescence system can be divided into Excited State Absorption (ESA), Energy Transfer Up-conversion (ETU) and Photon Avalanche (PA) roughly.⁴⁴ To our knowledge, there is a remarkable distinction in the absorption cross-section between Yb³⁺ and Er³⁺ ions,⁴⁵ and there is also a significant differences on the concentration of them in this work, which indicates that the UC luminescence of NaScF₄:10%Yb³⁺, 2%Er³⁺ should be principally contributed by the ETU mechanism. As



Fig. 6 The energy transfer mechanism between Yb^{3+} and Er^{3+} ions for UC luminescence.

Fig. 6 illustrated, the transition process takes place in the following steps:^{45, 46}

$${}^{2}F_{5/2}(Yb^{3+}) + {}^{4}I_{15/2}(Er^{3+}) \rightarrow {}^{2}F_{7/2}(Yb^{3+}) + {}^{4}I_{11/2}(Er^{3+})$$

$${}^{2}F_{5/2}(Yb^{3+}) + {}^{4}I_{11/2}(Er^{3+}) \rightarrow {}^{2}F_{7/2}(Yb^{3+}) + {}^{4}F_{7/2}(Er^{3+})$$

$${}^{2}F_{5/2}(Yb^{3+}) + {}^{4}I_{13/2}(Er^{3+}) \rightarrow {}^{2}F_{7/2}(Yb^{3+}) + {}^{4}F_{9/2}(Er^{3+})$$

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The excited Er^{3+} relaxes nonradiatively to its energy levels of ${}^{2}H_{11/2}/{}^{4}S_{3/2}$, then the instability of ${}^{2}H_{11/2}/{}^{4}S_{3/2}$ causes radiation transitions of ${}^{2}H_{11/2}/{}^{4}S_{3/2} \rightarrow {}^{4}I_{15/2}$ that shows a strong green emission (515~565 nm). In addition, a small part of the photoelectrons can be further filled to ${}^{4}F_{9/2}$ through non-radiative relaxation process, and which subsequently results in red emission (645~680 nm) by radiative transition of ${}^{4}F_{9/2} \rightarrow {}^{4}I_{15/2}$. Meantime, the electron on ${}^{4}I_{13/2}$ is excited to the ${}^{4}F_{9/2}$ state which also generates the abovementioned red emission. However, the prominent energy gap between ${}^{4}S_{3/2}$ and ${}^{4}F_{9/2}$ is disadvantageous to the non-radiation relaxation from ${}^{4}S_{3/2}$ to ${}^{4}F_{9/2}$, that's why the green emission is stronger than that of red (Figure 4).



Fig. 7 UC luminescence spectra of NaScF₄:10%Yb³⁺, 2%Er³⁺ phosphors with different surfactants under 980 nm NIR excitation (P = 0.944 W; I = 1.5 A).

Then we explored the luminescent properties of the NaScF₄:10%Yb³⁺, 2%Er³⁺ sample prepared using the three different surfactants mentioned previously. The spectral results are shown in Figure 7. All the testing conditions are the same (such as pump power, slit width, etc.), so it is easy to find that the sample prepared under EDTA has the highest luminous intensity when excited with 980 nm NIR (I = 1.5 A), which can be reasonably explained by the morphology/crystallinity in Figure 3. In general, the luminous intensity of the phosphors is related to the degree of surface defects of the crystal. The greater the degree of surface defects, the lower the luminescence intensity, and the surface defects are closely related to the specific surface area of the crystals, which tends to decrease as the specific surface area decreases.⁴⁷ It is well known that the specific surface area of a sample decreases as the crystal size increases, so that a large crystal size is advantageous for light emission because the surface defects are indirectly reduced. It can be seen from Fig. 3a-d that the crystal size is the largest and the crystallinity is the best under the condition of EDTA, so the luminescence intensity is naturally the strongest. The temperaturesensitive properties explored later have a certain relationship with the luminescent properties of the sample,⁴⁸ so the temperature sensing capability of the NaScF4:10%Yb3+, 2%Er3+ sample was subsequently investigated using EDTA.

3.3. Temperature sensing behavior

According to the knowledge we learned the leaved of the emission integral intensity ratio (rare earth ions) of the thermal coupling energy level and the temperature can be expressed as follows:⁴⁸

$$FIR = \frac{I_U}{I_L} = C * \exp\left(\frac{-\Delta E}{kT}\right)$$
(2)

Here, I_U and I_L represent the integral intensity of up and down emission peak in the thermal coupling energy levels; ΔE is for level spacing; T is for the absolute temperature of the sample; both C and k are constant, and C is related to the substrate material. Evidently, the two thermal coupling energy levels of Er^{3+} which point to ${}^{2}H_{11/2}$ and ${}^{4}S_{3/2}$ are close enough, this provides favorable conditions for the population of the thermal effect to be filled from the lower level to the upper level. The thermal effect of the laser can be effectively avoided by controlling the irradiation time of the laser, and the measurement current is only 1.5 A during the experimental test, which all laid the foundation to make the *FIR* only the function of temperature, then a reliable way is gained to test



the temperature sensitivity of the sample. The relationship of *FIR* and *T* can be deformed into the following expression:⁴⁸

$$In\left(\frac{I_U}{I_L}\right) = -\frac{\Delta E}{k} \cdot \frac{1}{T} + InC \qquad (3)$$

Fig. 8a shows the test results of the UC spectra of the sample under different temperatures, and a series of integrated intensity ratios of ${}^{2}H_{11/2} \rightarrow {}^{4}I_{15/2}$ to ${}^{4}S_{3/2} \rightarrow {}^{4}I_{15/2}$ can be calculated. Afterwards, the intercept and slope were obtained by linear fitting just like Fig. 8b, that is, 1.44±0.053 and -940.82±21.73 respectively. The Boltzmann constant *k* can be found in the database, it's easy to find the values of ΔE and *C* now, about 653.58 cm⁻¹ and 4.21 respectively.



Fig. 9 NaScF₄:10%Yb³⁺, 2%Er³⁺ prepared by using EDTA: (a) UC luminescence spectra at different temperatures; (b) The dependence of *FIR* on the temperature, and the inset displays UC emission spectra of green area at different temperatures.

And the second sample, EDTA was added during the preparation process on the basis of making other conditions consistent with the first sample. Next, this sample is fixed in the same position as the first sample, excited with the same pump power and measured its UC spectra at different temperatures. Eventually, an equivalent analysis and calculation were performed on it, and the results are shown in Fig. 9, in which the values of intercept and e_w slope are 1.67±0.036 and -1042.03±14.77 respectively. Therefore, C_{2}^{0} are 723.89 cm⁻¹ and C = 5.31 respectively.

The absolute sensitivity of a sample to temperature is usually expressed as S_A , which is an important indicator to measure the temperature sensitivity of the sample. The relationship among S_A , *FIR* and *T* can be expressed as:⁴⁹

$$S_A = \frac{\mathrm{d}(FIR)}{\mathrm{d}T} = C \cdot \frac{\Delta E}{\mathrm{k}T^2} \cdot \exp\left(\frac{-\Delta E}{\mathrm{k}T}\right) \qquad (4)$$

Based on the previous calculations, a series of S_A can be obtained by a simple substitution method. Fig. 10 shows the trend of sensitivity as a function of temperature. According to



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Fig. 10 The trend of absolute sensitivity as a function of temperature: (a) $NaScF_4$: $10\%Yb^{3+}$, $2\%Er^{3+}$ without EDTA; (b) $NaScF_4$: $10\%Yb^{3+}$, $2\%Er^{3+}$ with EDTA.

the experimental results, both the two samples reached the highest sensitivity at 548 K. According to the literature, it's meaningless to quantitatively compare the thermal sensitivity between thermometers with different properties based on different physical principles.⁵⁰ Therefore, we further calculated the relative sensitivity (S_R) of the two samples on the basis of the existing, and the definition of S_R is shown below:⁵¹

$$S_R = \frac{S_A}{FIR} \tag{5}$$

We calculated the S_R value and arranged the experimental optical thermometry parameters of the two samples in Table 1.

It is worth mentioning that the relative sensitivity values in Table 1 are of great significance for the evaluation of

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temperature uncertainty during temperature measurement, which is usually expressed as δT and the relationship between δT and S_R is as follows:⁵¹

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$$\delta T = \frac{\delta \Delta}{\Delta} \cdot \frac{1}{S_R} \tag{6}$$

Where $\delta\Delta/\Delta$ represents the relative uncertainty on Δ and it's usually taken as 0.03% for more sensitive detector. Now δT is mainly related to relative sensitivity. According to experimental calculation results, the maximum temperature uncertainty in the presence and absence of EDTA are 0.073 K and 0.095 K, respectively. This calculation result provides a more accurate quantitative basis for the investigation of the sample temperature sensing capability.

It can be seen that the sensitivity has improved by 30% after adding EDTA as a surfactant (Table 1). Previous studies have reported that the combination of rare earth ions with their ligands accounts for a large proportion of the sensitivityrelated factors; when combined by covalent bonding, the value of C can be used to measure the amount of covalent bond components roughly.⁴⁵ Assuredly, EDTA is a powerful complexing agent and it's a hexadentate ligand, then it can better guide the formation of covalent bonds during sample synthesis, which makes the increase in the value of C from 4.21 (Figure 8) to 5.31 (Figure 9).48 And as C increases, the covalent bond strengthens, which leads to enhance the temperature sensing capability of the product according to the previous formula (4).45,49 Additionally, a reasonable explanation can also be got from the crystallinity of the obtained samples. As shown in Figure S2, it is the XRD pattern of the NaScF₄:10%Yb³⁺, 2%Er³⁺ in the presence and absence of EDTA under the same test conditions, respectively. It can be seen that the diffraction peak of the sample is much higher under EDTA conditions, which reflects the higher crystallinity. As well known, the stronger the diffraction peak of the sample, the higher the crystallinity, and the stronger the luminescence performance.³¹ Therefore, the corresponding temperature sensitivity has been improved.49

Table. 1 Optical thermometry parameters of two samples in this work.

NaScF ₄ :Yb ³⁺ , Er ³⁺	<i>∆E</i> (cm⁻¹)	С	<i>S_{Amax}</i> (K ⁻¹)	<i>S_{Rmax}</i> (K ⁻¹)
Without EDTA	653.58	4.21	0.00256	0.00317
With EDTA	723.89	5.31	0.00328	0.00413

Finally, we compared the temperature sensitivity values of NaScF₄:Yb³⁺, Er³⁺ systems in the absence and presence of EDTA with some other reported materials,⁵³⁻⁵⁸ which are shown in Table 2. It can be seen that the temperature sensing capability of NaScF₄:Yb³⁺, Er³⁺system with EDTA is at a relatively high level.

Table.	2	А	portion	of	the	optical	thermometry	parametersclobathe
Yb ³⁺ /Er ³⁺ co-doped hosts. ⁵³⁻⁵⁸						DOI: 10.1039/D0DT00809E		

Host material	S _A max(K ⁻¹)	S _R max(K ⁻¹)
NaScF ₄ (without EDTA) ^{our work}	0.00256	0.00317
NaScF ₄ (EDTA) ^{our work}	0.00328	0.00413
NaYF ₄ ⁵³		0.00300
YF ₃ ⁵⁴	0.00260	
NaBiTiO ₃ ceramics ⁵⁵		0.00310
Fluorophosph glass 56	0.00150	
K ₃ Y(PO ₄) ₂ ⁵⁷	0.00304	0.00368
CaWO ₄ ⁵⁸	0.00250	

Conclusion

In general, Yb³⁺/Er³⁺ co-doped NaScF₄ particles were prepared by using distilled water as a single solvent, in which a higher concentration of Na⁺ (Na:Sc=9:1) was required to provide the driving force for the formation of NaScF₄ phase. In the process of the additive transforming from EDTA to SDBS and then to CA, the product morphology changed from short rods to granules and finally to clusters. Under the excitation of 980 nm NIR, the NaScF₄:Yb³⁺, Er³⁺ phosphors exhibited strong green and red emissions, and the up-conversion of their emissions were two-photon process. More importantly, we found that EDTA has a facilitating effect for the temperature sensing capability of NaScF₄:10%Yb³⁺, 2%Er³⁺ crystals and the temperature sensitivity value S_A/S_R increased from 0.00256 K⁻ ¹/0.00317 K⁻¹ to 0.00328 K⁻¹/0.00413 K⁻¹ after adding EDTA. And the maximum temperature uncertainty in the presence and absence of EDTA were 0.073 K and 0.095 K, respectively. It was concluded that NaScF₄:Yb³⁺, Er³⁺ systems have relatively superior temperature sensing capability and the present work may provide a new idea for the performance improvement of temperature sensitive materials.

Conflicts of interest

There are no conflicts of interest to declare.

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