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RESEARCH ARTICLE

NaYbF₄@NaYF₄ AS NEAR INFRARED LIGHT EXCITED INORGANIC OPTICAL SENSORS FOR OXYGEN-UNDISTURBED TEMPERATURE DETECTING

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ABSTRACT

The luminescence and temperature response characteristics of NaYF₄ containing 15% NaYbF₄ were investigated. NaYbF₄@NaYF₄ has good thermal stability and excellent response characteristics in the temperature in the range from 300 to 500 K, which significantly increases the upper limit of temperature detection of ytterbium temperature sensor. A self-calibration relationship between the reciprocal of temperature and the natural logarithm ratio of luminescent intensity has been discovered. Compared with the values of $\ln(I_{1048}/I_{976})$ or $\ln(I_{947}/I_{979})$ in Yb³⁺ emission spectra, the relationship between $\ln(I_{990}/I_{967})$ and $1/T$ is not linear, but exponential attenuation relationship with better temperature resolution near 400 K. Oxygen has no influence on these relations because of the ordered and dense crystal structure, which leading to the separation of Yb³⁺ and oxygen.

INTRODUCTION

Temperature is a basic thermodynamics variable in many fields of science and technology, which can be measured quantitatively by thermometers and sensors. Especially in bio systems, temperature is a significant parameter to characterize the physiological activities, such as the activities of proteins, the respiration and many other reactions. Among all the temperature sensors, optical thermometers especially luminescence sensors that based on various kinds of temperature-dependent physical properties have received abroad attentions because it is sensitive, can be applied to strongly colored or turbid media, and possesses many parameters (location of excitation wavelength λ_{ex} or emission wavelength λ_{em} , luminescence intensity I , luminescence quantum yields Φ , and luminescence lifetime τ) which are sensitive temperature (Kucsko *et al.*, 2013; Chen *et al.*, 2016). In many scientific and industrial areas, optical sensor technologies have been successfully deployed. However, to luminescence sensors, since the high atmospheric oxygen concentration and temperature-dependent gas diffusion, cross-sensitive to oxygen and temperature are usually unavoidable (Tang *et al.*, 2015; Stich *et al.*, 2008). Since temperature and oxygen are both important for all kinds of reactions, many researchers devoted themselves to design dual sensors for the two parameters. In 1999, Gouterman (Coyle and Gouterman, 1999) and coworkers use the lifetime of two probes (La₂O₂S:Eu³⁺ and PtTFPP) to detect the temperature and oxygen concentration, respectively.

Nevertheless, the luminescence quantum yields of the two probes were quite low, which greatly limited the application of this system. In 2006, Wolfbeis (Wolfbeis, 2006) and coworkers developed a dual sensor using a europium dye as a luminescent indicator for temperature and a palladium dye for oxygen. By complex iteration calculations, the composite material enabled simultaneous and contactless sensing of oxygen and temperature. The near infrared light (NIR, 750-1150 nm) is promising for developing bio-probes due to its deep penetration and less damage to tissues. Yb³⁺ can be excited from 800 to 1050 nm and emit NIR light from 900 to 1150 nm, the emission of Yb³⁺ is sensitive to temperature, all of which make it suitable for develop NIR excitation-emission temperature sensors (Newell *et al.*, 2007). Early in 1997, Baxter (Maurice *et al.*, 1997) and coworkers reported self-referenced point temperature sensor based on a fluorescence intensity ratio in Yb³⁺-doped silica fiber, but the influence of oxygen was not been estimated. Among the Yb³⁺ luminescence materials, the intense researches for NaYbF₄ have made it to be one of the best choices as nano-crystal hosts (Pan *et al.*, 2013). NaYbF₄ or NaYb_xY_yF₄ can provide intense luminescence for Ln³⁺ ions with high luminescence efficiency, especially for up-conversion emission to Er³⁺, Tm³⁺, Tb³⁺, etc (Zhou *et al.*, 2014). However, few attentions had been made to the individual luminescence properties of Yb³⁺. In 2017, Cao and coworkers used NaYbF₄ nanoparticles as NIR excited inorganic photosensitizers and investigated the transition probability from Yb³⁺ to oxygen at room temperature (Zhang *et al.*, 2017). Consequently, it is an attractive and challenge subject to investigate the photophysical temperature sensitive properties and the influence of oxygen of NaYbF₄ or NaYb_xY_{1-x}F₄. In this work, we investigated the properties of inorganic rare earth material NaYF₄ with partly of the substitution of Y³⁺ in the crystal lattice by Yb³⁺ (NaYbF₄@NaYF₄).

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$\text{NaYbF}_4@/\text{NaYF}_4$ could be excited by 808 nm NIR laser, and displayed the characteristic NIR emission band ranging from 900 to 1150 nm, which could be attributable to the ${}^2\text{F}_{5/2}$ to ${}^2\text{F}_{7/2}$ transition of Yb^{3+} . In contrast to organic ytterbium thermometers, we successfully raised the temperature-detective ceiling to 500 K and oxygen concentration has no influence on the NIR emission spectrum and temperature response of $\text{NaYbF}_4@/\text{NaYF}_4$.

Experimental Section

Preparation of $\text{NaYbF}_4@/\text{NaYF}_4$: All of the chemicals were analytical grade reagents purchased from Sigma-Aldrich. NaF (14.4 mmol, 0.605 g) was added to a stirred solution consist of $\text{Y}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ (0.36 mmol, 0.138 g), $\text{Yb}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ (0.12 mmol, 0.054g), sodium citrate (2.4 mmol, 0.706g) in ultrapure water (30 mL) in a 60 mL high pressure reactor. Once the entire solid have dissolved, ethyl acetate (10 mL) was added dropwise. After 45 minutes microwaving with stirring at 200 °C under N_2 , cooled to room temperature. The suspension was then centrifuged, and the precipitate was washed with distilled water and ethanol for three times respectively, and then dried at 300 °C for 5h on muffle.

Characterizations: X-ray diffraction (XRD) patterns were measured on a Rigaku D/MAX-PC 2500 diffractometer with monochromatic Cu $\text{K}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$) at an accelerating potential of 40 kV and a tube current of 300 mA. UV-Vis absorption measurements were carried out on an absorption spectrometer (PE). Fluorescence emission and excitation spectra and the influence of temperature on the luminescence properties under different atmospheres were measured using an Edinburgh FLS 980 spectrophotometer equipped with an Oxford Optistat DN2 cryostat.

RESULT AND DISCUSSION

Dynamic range is referred to the range between the lowest and the highest temperature that can be determined with adequate precision. For organic thermometer, the dynamic range of temperature is restricted to the thermal stability of component organic compounds and polymers host matrix. According to a previously reported method with some modifications (see experimental section), we synthesized an inorganic rare earth material $\text{NaYbF}_4@/\text{NaYF}_4$. The X-ray diffraction (XRD) of $\text{NaYbF}_4@/\text{NaYF}_4$ is illustrated in Fig. 1. The XRD patterns suggest that there exist a mix of NaYbF_4 (hcp) and NaYF_4 (hcp). We can clearly observe the radiative deactivation from the excited-state ${}^2\text{F}_{5/2}$ level to excited-state ${}^2\text{F}_{7/2}$ level in $\text{NaYbF}_4@/\text{NaYF}_4$ fluorescence absorption and emission spectra (Fig. 2), and the relative populations of the sublevels can be described by Boltzmann distribution. Figure 2a shows the absorption spectra of $\text{NaYbF}_4@/\text{NaYF}_4$. The maximum absorption wavelength of $\text{NaYbF}_4@/\text{NaYF}_4$ is 970 nm (${}^2\text{F}_{7/2}^a \rightarrow {}^2\text{F}_{5/2}^a$), and there is a weak absorption bank at 808 nm (${}^2\text{F}_{7/2}^a \rightarrow {}^2\text{F}_{5/2}^c$). Upon light excitation of Yb^{3+} by 808 nm of AlGaAs semiconductor laser diode pumping, $\text{NaYbF}_4@/\text{NaYF}_4$ displays the characteristic ${}^2\text{F}_{5/2} \rightarrow {}^2\text{F}_{7/2}$ transition of Yb^{3+} emission ranging from 900 to 1150 nm with the maximum peak at 967 nm (Fig. 2b). The influences of temperature and oxygen concentration on the luminescence of $\text{NaYbF}_4@/\text{NaYF}_4$ are shown in Figure 3. $\text{NaYbF}_4@/\text{NaYF}_4$ displays a trend of decreasing intensities and quantum yields with temperature increasing no matter under nitrogen or oxygen (Figure 3a, 3b), which has been a basis for developing luminescence thermometers.

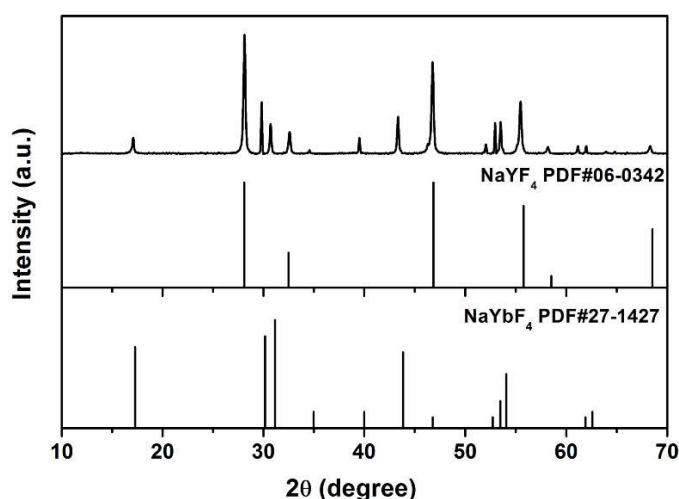


Figure 1. XRD of $\text{NaYbF}_4@/\text{NaYF}_4$, JCPDS No. 06-0342 and 27-1427

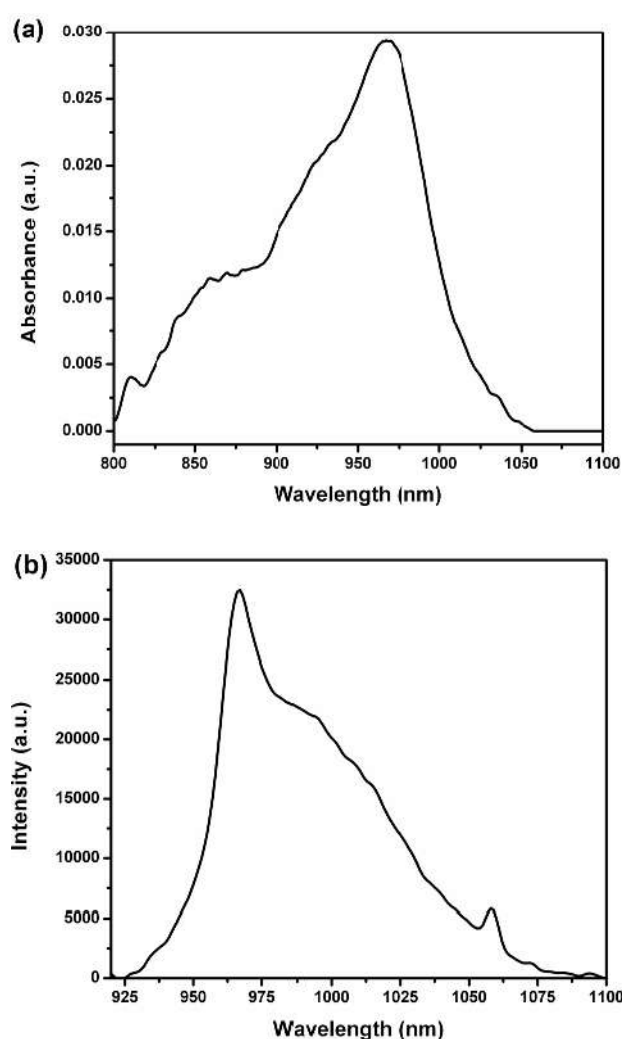


Figure 2. Spectra of $\text{NaYbF}_4@/\text{NaYF}_4$ under air at 298 K (a) absorption spectra and (b) luminescence emission spectrum ($\lambda_{\text{ex}} = 808 \text{ nm}$)

It is also interesting to find that the normalized Yb^{3+} luminescence spectra of $\text{NaYbF}_4@/\text{NaYF}_4$ are almost the same shape in the wavelength range from 920 to 1100 nm under the different atmospheres (Figure 3c, 3d), which indicates that O_2 concentration does not influence on the emission process or the corresponding irradiation transition of $\text{NaYbF}_4@/\text{NaYF}_4$.

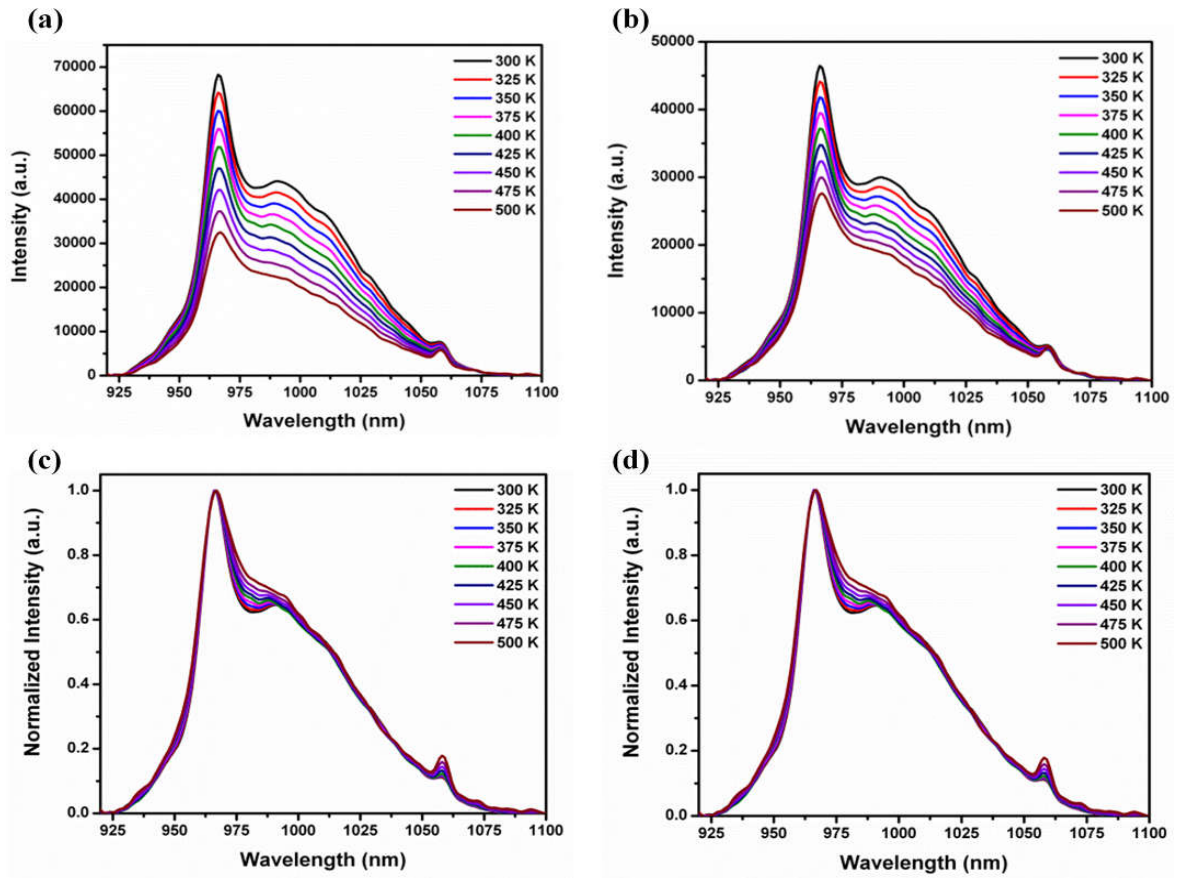


Figure 3. The luminescence properties of NaYbF₄@NaYF₄ ($\lambda_{ex} = 808$ nm). (a) Luminescence spectra under nitrogen. (b) Luminescence spectra under oxygen. (c) Normalized luminescence spectra under nitrogen. (d) Normalized luminescence spectra under oxygen

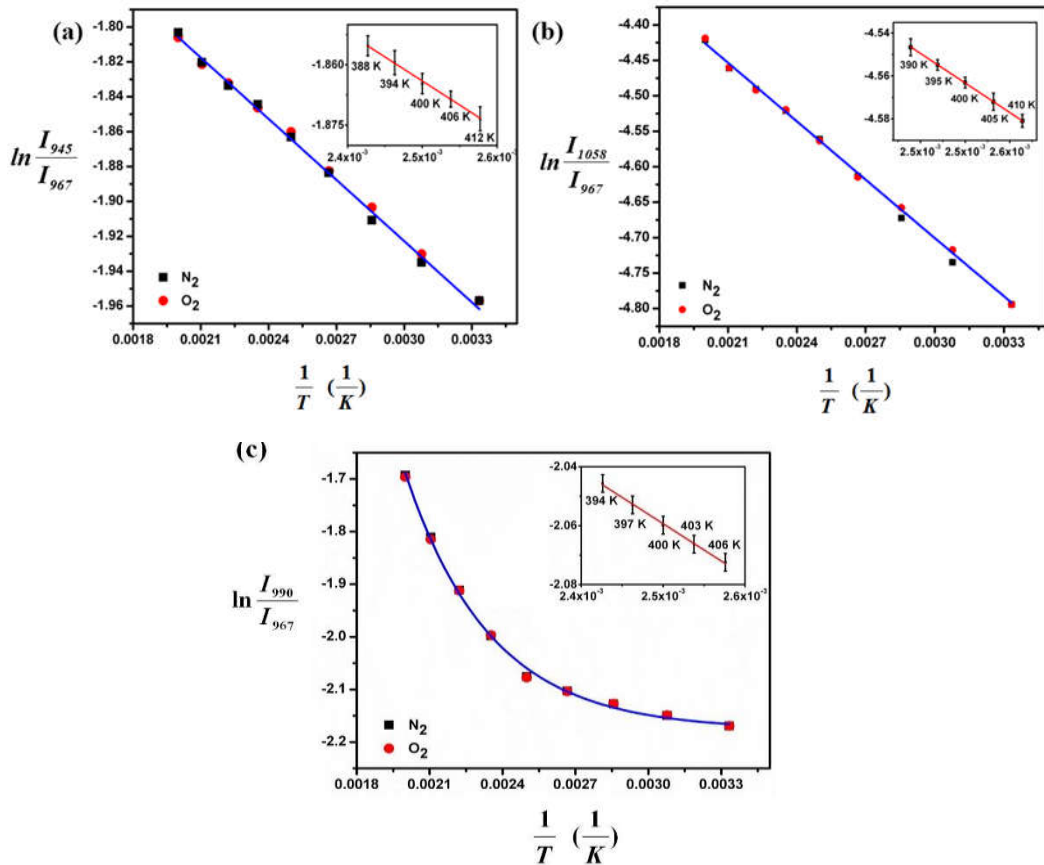


Figure 4. The temperature sensing properties of NaYF₄ (containing 15% Yb) in N₂ and O₂ in the range from 300 to 500 K. (a) The plot of $\ln(I_{945}/I_{967})$ versus $1/T$ (Inset: The plot of $\ln(I_{945}/I_{967})$ to the temperature variation around 400 K) (b) The plot of $\ln(I_{1058}/I_{967})$ versus $1/T$ (Inset: The plot of $\ln(I_{1058}/I_{967})$ to the temperature variation around 400 K). (c) The plot of $\ln(I_{990}/I_{967})$ versus $1/T$ (Inset: The plot of $\ln(I_{990}/I_{967})$ to the temperature variation around 400 K)

We infer that it is the ordered and dense crystal structure that isolated oxygen and the Yb^{3+} in the lattice, which lead to the similar luminescence spectra of Yb^{3+} in different atmosphere. In our previous work, we reported a self-calibration relationship between the reciprocal of temperature ($1/T$) and the natural logarithm ratio of luminescence intensity (I) (Tang *et al.*, 2015; Wang *et al.*, 2016). It was found that the value of $\ln I$ ratio in NIR range of the Yb^{3+} emission linearly decreased with the increase of $1/T$ in a wide range, which well obeyed the Arrhenius equation. As for $\text{NaYbF}_4@/\text{NaYF}_4$, both the plots of $\ln(I_{945}/I_{967})$ and $\ln(I_{1058}/I_{967})$ versus $1/T$ are also straight lines in the range from 300 to 500 K and overlap with each other as we have expected (Figure 4a, 4b), because of the separation of Yb^{3+} and O_2 . The resolution to temperature variation around 400 K of these plots are 6 K and 5 K, respectively (Figure 4a and 4b inset). To our surprise, the plots of $\ln(I_{990}/I_{967})$ versus $1/T$ are not straight lines, but an exponential decay in the range from 300 to 500 K with a resolution to temperature variation to be better than 3 K around 400 K (Figure 4c). Because the location of 990 nm is the overlapped region of three banks ($^2\text{F}_{5/2}^a \rightarrow ^2\text{F}_{7/2}^a$, $^2\text{F}_{5/2}^b \rightarrow ^2\text{F}_{7/2}^c$ and $^2\text{F}_{5/2}^a \rightarrow ^2\text{F}_{7/2}^b$), we infer that the variation of the intensities and half-peak widths of the two banks with temperature might lead to the exponential decay and better resolution. Further investigation on the application of these temperature sensors is going on in our laboratory.

Conclusion

In summary, we study the luminescent and temperature-response properties of NaYF_4 containing 15% NaYbF_4 . $\text{NaYbF}_4@/\text{NaYF}_4$ is thermally stable and exhibit an excellent response in the temperature range from 300 K to 500 K, which significantly raised the temperature-detective ceiling than that of organic ytterbium complexes sensor. Compare to the $\ln(I_{1048}/I_{967})$ or $\ln(I_{945}/I_{967})$ value in the Yb^{3+} luminescence spectrum, $\ln(I_{990}/I_{967})$ versus $1/T$ is not a linear relation, but an exponential decay with a better temperature resolution about 3 K around 400 K. Oxygen has no influence on these relations because of the ordered and dense crystal structure that leading to the separation of Yb^{3+} and oxygen.

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