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**A Strategy for Enhancing the Sensitivity of Optical Thermometer in β-NaLuF₄:Yb³⁺/Er³⁺ Nanocrystals**

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A strategy for enhancing the sensitivity of optical thermometer is developed here by using non-thermal coupled levels of Er³⁺. Under the excitation of 980 nm laser, the temperature dependence of 244 nm and 256 nm upconversion luminescences (UCLs) of Er³⁺ were studied. The corresponding ⁴I₁₁/₂ and ⁴D₇/₂ levels are confirmed to be non-thermally coupled levels. By using fluorescence intensity ratio (FIR) technique and investigating different thermal population behaviors of ⁴I₁₁/₂ and ⁴D₇/₂ levels, optical temperature sensing performance based on non-thermal coupled levels of Er³⁺ was fulfilled here for the first time. The obtained maximum sensor sensitivity is 0.106 K⁻¹ at 525 K, much higher than those of all other RE³⁺ doped optical thermometer using thermal coupled levels-based FIR technique. This suggests that the use of FIR from neighboring non-thermal coupled levels of RE³⁺ is a promising approach for enhancing the sensor sensitivity of optical thermometers.

**Introduction**

High accuracy and high resolution temperature measurement is a challenging research topic in both scientific and industrial fields.¹⁻⁴ Because of the noninvasive mode and quick response, luminescence-based measurement is one of the most important technologies for determining temperature.⁵⁻⁸ Recently, non-contact optical temperature sensors based on the fluorescence intensity ratio (FIR) among different emission lines have attracted much interest due to their excellent sensitivity and accuracy.⁹⁻¹⁸ Moreover, compared with other temperature measurement techniques, this optical thermometry method can reduce the dependence of testing condition, such as fluorescence loss and electromagnetic compatibility problem, resulting in its potential applications in biocompatible temperature probe, electrical power stations, coal mines, and oil refineries, etc.¹⁹⁻²²

Rare earth ions (RE³⁺) have multiple energy level structures, the interest in RE³⁺ doped upconversion luminescent (UCL) nanoparticles has experienced a surge within the scientific community owing to the near-infrared (NIR) excitation source and their unique optical characteristics arising from their intra 4f transitions.²³⁻³⁸ In addition, by investigating the energy level distributions of RE³⁺ ions, we find Er³⁺, Tm³⁺, Ho³⁺, Gd³⁺, Pr³⁺, and Nd³⁺, etc., have pairs of thermally coupled levels, made them potentially candidates for optical thermometry by using FIR technique. As one of the most important RE³⁺, Er³⁺ has abundant and ladder-like energy level structure, which is an ideal activator for UCL. More importantly, over the past few years, Er³⁺ doped UCL materials have been widely considered as optical temperature sensor by comparing the emission intensities from thermally coupled electronic levels of ⁴I₁₁/₂ and ⁴S₃/₂.³⁹⁻⁴¹ As we know, Er³⁺ ions have multiple energy level structures in ultraviolet (UV) region. The UV UCLs of Er³⁺ under the excitation of NIR laser have been reported in fluoride nano/microparticles in our previous works.⁴², ⁴³ However, heretofore few results on optical thermometry have been reported mainly concerning the UCLs of Er³⁺ in the UV region.⁴⁴, ⁴⁵

Generally, the FIR method is implemented by exploiting the temperature-dependent luminescence intensities from two nearby electronic energy levels which are governed by Boltzmann-type population distribution. It is known that the fluorescence intensities are proportional to the population of two thermally equilibrivous levels, thus, the FIR can be expressed by \( C \exp(-\Delta E/kT) \), where \( C \) is a constant, \( \Delta E \), \( k \), and \( T \) represent the energy difference between the two nearby levels, the Boltzmann constant, and the absolute temperature, respectively. According to the principle of a FIR-based optical thermometer, the sensor sensitivity, which is an important parameter to determine the performance of temperature sensor, is proportional to the energy gap of the corresponding thermally coupled energy levels. As we all know, the larger energy gap is the higher sensor sensitivity is. However, to ensure the upper level of optical activators (RE³⁺) is thermally populated from their lower levels, the energy difference between the emitting levels of RE³⁺ ions is upper bounded at
about 2000 cm⁻¹. Although the highest sensitivity has reached 2.8 × 10⁻⁴ K⁻¹ in NaYF₃:Nd³⁺ microcrystals by using thermal coupled levels of Nd³⁺, further enhancement of the sensing sensitivity is difficult to implement owing to the restriction of energy gap between thermal coupled levels, as mentioned above.

Herein, we presented a strategy for enhancing the sensitivity of temperature sensor by virtue of the non-thermally coupled levels of Er³⁺. Hexagonal phase (β-) NaLuF₄ was chosen as the matrix material in this work. Upon excitation with 980 nm NIR laser, UC emissions of Er³⁺ in the UV region of 235 ~ 270 nm were investigated. The luminescence intensity ratios of 244 nm to 256 nm of Er³⁺ were discussed systematically by changing the sample temperature. The related thermal behaviors originating from the ²I₁₁/₂ and ⁴D₁₂ states of Er³⁺ were investigated in the temperature range of 300 ~ 525 K. A high sensitivity was achieved in this UV-based sensor by using non-thermally coupled levels (²I₁₁/₂ and ⁴D₁₂) of Er³⁺. The highest sensor sensitivity reached 0.106 K⁻¹ in this work, which is prior to all previously reported RE³⁺ doped temperature sensor by exploiting the thermal coupled levels-based FIR technique. This novel temperature sensing performance based on the non-thermally coupled levels of Er³⁺, combined with their imaging characteristics, made Er³⁺-based UV UCL materials promising platforms for potential biological applications.

Experimental procedures

Chemicals

The raw chemicals, including LuCl₃·6H₂O, YbCl₃·6H₂O, ErCl₃·6H₂O (all with purity > 99.999%, Shanghai Shabo Chemical Technology Co., Ltd. China), NaOH, NH₄F (all with the analytically purity, Beijing Fine Chemical Company, China), 1-Octadecene (ODE, 90%, Alfa Aesar) and oleic acid (OA, 90%, Alfa Aesar) were used without further purification.

Sample Preparation

NaLuF₄:Yb³⁺/Er³⁺ sample was prepared via a thermal decomposition method, which described briefly as follows. In a typical procedure for the synthesis of NaLuF₄:20%Yb³⁺, 1.5%Er³⁺, 1 mmol RECl₃·6H₂O (RE = Lu, Yb, Er) were added to a 100 mL three-neck round-bottom flask containing a certain amount of ODE and OA. The solution was magnetically stirred and heated to 150 °C for 30 min to remove residual water and oxygen. Then, the temperature was cooled down to room temperature with a gentle flow of argon gas through the reaction flask. Meanwhile, a solution of NH₄F and NaOH dissolved in methanol was added, and then the temperature was increased to 50 °C. After methanol was evaporated, the reaction mixture was heated to 300 °C in an argon atmosphere, kept for 60 min and then naturally cooled to room temperature. The resultant products were precipitated by the addition of ethanol, collected by centrifugation and washed with ethanol three times.

Characterizations

The crystal structure were analyzed by a Rigaku RU-200b X-ray powder diffractometer (XRD) using a nickel-filtered Cu-Kα radiation (λ = 1.5406 Å). The size and morphology of the sample were investigated by transmission electron microscopy (TEM, Hitachi H-600). The UCL spectra were recorded using a Hitachi F-4500 fluorescence spectrophotometer which equipped with a power-controllable 980 nm CW diode laser as excitation source. The temperature of the sample was controlled by using a set of home-made equipment.

Results and discussion

Figure 1(a) shows the XRD pattern of the sample. It is clear that the sample was β-NaLuF₄, which was in good agreement with the standard values of JCPDS No.27–726. The morphological analysis of the sample with TEM, as depicted in Fig. 1(b), showed that the as-synthesized NaLuF₄:Yb³⁺/Er³⁺ nanoparticles were approximately spherical with nearly uniform size distribution. The diameters of NaLuF₄ nanospheres were about 40 nm on average.

Fig. 1 (a) XRD pattern of NaLuF₄:Yb³⁺/Er³⁺ nanocrystals and the standard datum for hexagonal phase NaLuF₄ (JCPDS No.27-726); (b) TEM image of NaLuF₄:Yb³⁺/Er³⁺ nanocrystals.

At 980 nm excitation of ~300 mW, the NaLuF₄:Yb³⁺/Er³⁺ nanocrystals emitted UC luminescence in UV region, as shown in Fig. 2. Two characteristic emissions in the range of 235 ~ 271 nm were observed. The UC emissions that centered at 244 nm and 256 nm originated from the ²I₁₁/₂ → ⁴I₁₅/₂ and ⁴D₂ → ²I₁₅/₂ transitions of Er³⁺, respectively.²⁴, ⁴⁶ In Yb³⁺/Er³⁺ codoped NaLuF₄ nanocrystals, the successive energy transfer (ET) from Yb³⁺ ions to Er³⁺ is crucial important for populating the high energy states of Er³⁺. Figure 3 gives the possible UC population ways in energy level diagrams of Yb³⁺ and Er³⁺ ions.⁴⁸ The population processes for the UV (²I₁₁/₂ and ⁴D₂) levels of Er³⁺ can be clearly described as:

\[ \text{NR} \rightarrow ²H₁₁/₂ \rightarrow ⁴S₂ \rightarrow ²G₇/₂ \rightarrow ⁴F₇/₂ \]

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Fig. 2 UC emission spectrum of β-NaLuF₄:Yb³⁺/Er³⁺ nanocrystals in the range of 235 – 271 nm.

To investigate the thermally population behaviors of the ²⁷I₁₁/₂ and ⁴D₇/₂ levels of Er³⁺, the 244 nm and 256 nm UC emissions were discussed by a change of sample temperature from 300 K to 525 K. Figure 4(a) displays the corresponding temperature-dependent UCL spectra of NaLuF₄:Yb³⁺/Er³⁺ nanocrystals. There was nearly no overlap of emission bands from the ²⁷I₁₁/₂ → ²⁷I₁₅/₂ and ⁴D₇/₂ → ⁴I₁₅/₂ transitions of Er³⁺, which was benefit for the measuring accuracy of their emission intensities. Additionally, it is obvious that the emission intensities from 244 nm and 256 nm changed greatly with the enhancement of sample temperature.

The detailed variation of the integrated emission intensities of I₂₄₄ and I₂₅₆, as calculated from the UCL spectra, is shown in Fig. 4(b). Obviously, the emission intensity of I₂₅₆ is stronger than that of I₂₄₄ in the whole investigated temperature range. In addition, both the I₂₄₄ and I₂₅₆ decreased with increasing the sample temperature from 300 K to 525 K, which is mainly attributed to the thermal quenching.

Fig. 3 Energy level diagrams of Yb³⁺ and Er³⁺ ions as well as the proposed UC processes.

\[ ²H₀₂ \xrightarrow{\text{ET}} ²D₀₂ \xrightarrow{\text{NR}} ²K₁₃/₂ \xrightarrow{\text{ET}} ²I₁₃/₂ \xrightarrow{\text{NR}} ⁴D₇/₂ \]

where NR represents the nonradiative relaxation from excited Er³⁺ to their lower levels.

Fig. 4 (a) Temperature-dependent UCL spectra of β-NaLuF₄:Yb³⁺/Er³⁺ nanocrystals in the range of 235 – 271 nm; (b) Temperature-dependent integrated emission intensities of ²⁷I₁₁/₂ → ⁴I₁₅/₂ and ⁴D₇/₂ → ⁴I₁₅/₂ transitions of Er³⁺.

For clarity, all UCL spectra in Fig. 4(a) have been normalized to compare the relative intensity ratio between the two transitions. The temperature-dependent population processes of ²⁷I₁₁/₂ and ⁴D₇/₂ levels of Er³⁺ are non-thermally coupled levels. To further investigate the temperature-dependent population processes of ²⁷I₁₁/₂ and ⁴D₇/₂ levels, we calculated the intensity change ratio of I₂₄₄ (²⁷I₁₁/₂ → ²⁷I₁₅/₂) and I₂₅₆ (⁴D₇/₂ → ⁴I₁₅/₂) of Er³⁺, as depicted in Fig. 5(b). Here, the intensity change ratio is defined as (I₀/Iₙ)/I₀, where I₀ and I are the UC emission intensities before and after the temperature changes, respectively. (i.e., I₀ and I are the UC emission intensities recording at 325 K and 350 K, respectively, for the data point at 350 K in Fig 5(b)). As such, it is worthwhile to point out that the intensity change ratios of these two transitions are different. The intensity change ratio of ²⁷I₁₁/₂ → ²⁷I₁₅/₂ transition of Er³⁺ are larger than that of their ⁴D₇/₂ → ⁴I₁₅/₂ transition in the whole temperature range, as depicted in Fig 5(b), and the corresponding explanation is described below.
Hence, the total population of Er\(^{3+}\) with thermal quenching, the NR process of Er\(^{3+}\) is thermally populated from their lower states to the enhanced population of Er\(^{3+}\) in \(\beta\)-NaLuF\(_4\):Yb\(^{3+}\)/Er\(^{3+}\) nanocrystals as well as fitting result.

As shown in Fig. 4(b), both the \(I_{244}\) and \(I_{256}\) decreased with increasing the sample temperature, as displayed in Fig. 4(b). From the energy level diagram as displayed in Fig. 3, there is a nonradiative relaxation process from \(2\text{I}_{11/2}\) to \(4\text{D}_{7/2}\) levels of Er\(^{3+}\), thus, the upconverted population from these two states can be affected by the sample temperature. The higher temperature is the larger multiphonon relaxation rate of \(2\text{I}_{11/2}\) to \(4\text{D}_{7/2}\) is. As a result, the UC emissions from \(2\text{I}_{11/2}\) to \(4\text{D}_{7/2}\) decreased and enhanced, respectively, due to the effective NR process as sample temperature increased from 300 K to 525 K. However, compared with thermal quenching, the NR process of \(2\text{I}_{11/2}\) to \(4\text{D}_{7/2}\) played a relatively small effect on the population of \(2\text{D}_{7/2}\) level of Er\(^{3+}\). Hence, the total population of \(2\text{D}_{7/2}\) state decreased gradually with increasing the sample temperature, as displayed in Fig. 4(b). Furthermore, as reported in our previous work, the \(4\text{D}_{7/2}\) state of Er\(^{3+}\) was thermally populated from their lower \(4\text{G}_{9/2}\) level, leading to the enhanced population of \(2\text{D}_{7/2}\) level with the increase of sample temperature as well. To sum up, during the upconverted population processes, the nonradiative relaxation and the thermally populated process worked simultaneously, resulting in the intensity change ratios of 244 nm (\(2\text{I}_{11/2}\) to \(2\text{I}_{15/2}\)) UC emissions are larger than those of 256 nm (\(2\text{D}_{7/2}\) to \(2\text{I}_{15/2}\)). Just because of the different temperature-dependent variation properties of 244 nm and 256 nm UCLs of Er\(^{3+}\), their \(2\text{I}_{11/2}\) and \(2\text{D}_{7/2}\) levels can be used as thermally-related levels to detect temperature by using FIR method.

Figure 6 shows the change of FIR of UV UCLs \((I_{236}/I_{244})\) of Er\(^{3+}\) with increasing the absolute temperature from 300 K to 525 K. By fitting data points according to the equation of \(\text{Cexp}(\Delta E/kT)\), the obtained values of C and \(\Delta E\) were about 1715 and 449 cm\(^{-1}\), respectively. Notably, the slope of the fitting curve increased gradually with the enhancement of sample temperature, as shown in Fig. 6. To further investigate the temperature sensing performance, it is critical for us to discuss the sensor sensitivity \(S\) for an optical thermometer. The rate in which FIR varies with absolute temperature, i.e. \(S\), can be defined as:

\[
S = \frac{\Delta[I\text{FIR}]}{\Delta T} = \frac{\Delta[I\text{FIR}]}{\Delta T}.
\]

The corresponding sensitivity curve of this non-thermal coupled levels-based sensor is given in Fig. 7. Obviously, the sensor sensitivity increased dramatically with the enhancement of sample temperature. The value of \(S\) reached the maximum of 0.106 K\(^{-1}\) at 525 K. A cycle test with high repeatability was obtained in NaLuF\(_4\):Yb\(^{3+}\)/Er\(^{3+}\) nanocrystals. To our knowledge, it is the first time that optical thermometer was obtained by using the non-thermally coupled UV levels of Er\(^{3+}\) ions.
At last, it is critical to compare the sensitivity of this optical thermometer with those of other RE$^{3+}$-based temperature sensors. Table 1 lists the sensitivities of several typical temperature sensors based on FIR technique doped with different RE$^{3+}$ ions. It is noteworthy that all the sensor sensitivities are detected by using thermal coupled levels of RE$^{3+}$ except for this work, where the sensitivity is obtained by virtue of the $^{2}I_{11/2}$ and $^{4}D_{2}$ non-thermally coupled levels of Er$^{3+}$. From Table 1, we found that the sensitivity achieved in this work is the highest among all sensors. Therefore, we concluded that the use of non-thermally coupled levels of Er$^{3+}$ is an effective approach to enhance the sensor sensitivity of optical thermometers.

<table>
<thead>
<tr>
<th>Ions (host)</th>
<th>Transitions</th>
<th>$S_{\text{max}}$ (10$^{-4}$K$^{-1}$)</th>
<th>Temperature Range (K)</th>
<th>Reference</th>
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<tr>
<td>Gd (β–NaLuF$_4$)</td>
<td>$^{6}P_{5/2}, ^{6}P_{3/2} \rightarrow ^{8}S_{3/2}$</td>
<td>4.05</td>
<td>298 – 523</td>
<td>14</td>
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<td>Er (fluorotellurite glass)</td>
<td>$^{2}H_{11/2}, ^{4}S_{3/2} \rightarrow ^{4}I_{15/2}$</td>
<td>54</td>
<td>300 – 550</td>
<td>19</td>
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<td>Er-Mo (Yb$_3$Al$<em>5$O$</em>{12}$)</td>
<td>$^{2}H_{11/2}, ^{4}S_{3/2} \rightarrow ^{4}I_{15/2}$</td>
<td>48</td>
<td>295 – 973</td>
<td>36</td>
</tr>
<tr>
<td>Er (LiNbO$_3$)</td>
<td>$^{2}H_{11/2}, ^{4}S_{3/2} \rightarrow ^{4}I_{15/2}$</td>
<td>121</td>
<td>285 – 453</td>
<td>35</td>
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<tr>
<td>Er (CaWO$_4$)</td>
<td>$^{4}G_{11/2}, ^{2}H_{9/2} \rightarrow ^{4}I_{15/2}$</td>
<td>190</td>
<td>300 – 873</td>
<td>40</td>
</tr>
<tr>
<td>Nd (glass ceramic)</td>
<td>$^{4}F_{5/2}, ^{4}F_{3/2} \rightarrow ^{4}I_{8}$</td>
<td>15</td>
<td>300 – 700</td>
<td>48</td>
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<tr>
<td>Nd (β–NaYF$_3$)</td>
<td>$^{4}F_{5/2}, ^{4}F_{3/2} \rightarrow ^{4}I_{8}$</td>
<td>280</td>
<td>323 – 673</td>
<td>42</td>
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<tr>
<td>Ho (Y$_2$O$_3$)</td>
<td>$^{3}K_{3}, ^{5}F_{3} \rightarrow ^{3}I_{8}$</td>
<td>30.2</td>
<td>299 – 673</td>
<td>49</td>
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<tr>
<td>Ho (β–NaLuF$_4$)</td>
<td>$^{5}F_{3}^2, ^{5}G_{5/2} \rightarrow ^{3}I_{6}$</td>
<td>14</td>
<td>390 – 780</td>
<td>50</td>
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<td>Ho (glass ceramic)</td>
<td>$^{5}F_{3}^2, ^{5}G_{5/2} \rightarrow ^{3}I_{6}$</td>
<td>1.21</td>
<td>303 – 643</td>
<td>51</td>
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<td>Tm (LiNbO$_3$)</td>
<td>$^{3}F_{2,3}, ^{3}H_{4} \rightarrow ^{3}H_{6}$</td>
<td>0.12</td>
<td>323 – 733</td>
<td>52</td>
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<td>Dy (Y$_2$Al$<em>5$O$</em>{12}$)</td>
<td>$^{4}I_{15/2}, ^{4}S_{9/2} \rightarrow ^{6}H_{15/2}$</td>
<td>30</td>
<td>296 – 973</td>
<td>53</td>
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<tr>
<td>Pr (NaYF$_3$)</td>
<td>$^{3}P_{0}, ^{3}P_{1} \rightarrow ^{3}H_{5}$</td>
<td>135.2</td>
<td>100 – 300</td>
<td>54</td>
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<td>Er (β–NaLuF$_4$)</td>
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<td>1060</td>
<td>300 – 525</td>
<td>this work</td>
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</table>

Table 1 Sensitivities of optical temperature sensors based on the fluorescence of materials with RE$^{3+}$ as activators.

Conclusions

In conclusion, a strategy for enhancing the sensitivity of optical temperature sensor is put forward here by using the FIR between non-thermal coupled levels of Er$^{3+}$. Under 980 nm laser excitation, UV UCLs from the $^{2}I_{11/2} \rightarrow ^{4}I_{15/2}$ (244 nm) and $^{4}D_{2} \rightarrow ^{4}I_{15/2}$ (256 nm) transitions of Er$^{3+}$ ions were observed in Yb$^{3+}$-Er$^{3+}$ codoped β-NaLuF$_4$ nanocrystals. By investigating their different thermal population behaviors, optical temperature sensing performance based on the non-thermal coupled levels of $^{2}I_{11/2}$ and $^{4}D_{2}$ was fulfilled in this work for the first time. The obtained maximum sensor sensitivity is 0.106 K$^{-1}$ at 525 K, which is prior to those of other RE$^{3+}$-based optical thermometer by using thermal coupled levels-based FIR technique. This excellent temperature sensing performance based on the UV UCLs of Er$^{3+}$, combined with their imaging characteristics, made Er$^{3+}$-based UCL materials potential candidates for multifunctional biomedical applications.

Acknowledgments

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Notes and references
