

ORIGINAL ARTICLE

Multifunctional optical thermometry based on the stark sublevels of Er^{3+} in $\text{CaO-Y}_2\text{O}_3$: $\text{Yb}^{3+}/\text{Er}^{3+}$

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Abstract

A conventional high temperature solid state method was utilized to prepare $\text{CaO-Y}_2\text{O}_3$, which is a potential candidate for manufacturing crucible material to melt titanium and titanium alloys with low cost. Meanwhile, Yb^{3+} ions and Er^{3+} ions were selected as the sensitizers and activators respectively to dope into $\text{CaO-Y}_2\text{O}_3$, aimed at providing real-time optical thermometry during the preparation process of titanium alloys realized using fluorescence intensity ratio (FIR) technology. The results reveal that a high measurement precision can be acquired by using the Stark sublevels of $\text{Er}^{3+} {}^4\text{F}_{9/2}$ to measure the temperature with a maximum absolute error of only about 3 K. In addition, by analyzing the dependence of ${}^4\text{I}_{13/2} \rightarrow {}^4\text{I}_{15/2}$ transition on pump power of 980 nm excitation wavelength, it was found that the laser-induced thermal effect has almost no influence on the temperature measurement conducted by using the FIR of the Stark sublevels of $\text{Er}^{3+} {}^4\text{I}_{13/2}$, which means that a high excitation pump power can be used to obtain strong NIR emission and good signal-to-noise ratio for optical thermometry without the influence of the laser-induced thermal effect. All the results reveal that $\text{CaO-Y}_2\text{O}_3$: $\text{Yb}^{3+}/\text{Er}^{3+}$ is an excellent temperature sensing material with high measurement precision.

KEYWORDS

fluorescence intensity ratio, optical thermometry, upconversion, $\text{Yb}^{3+}/\text{Er}^{3+}$

1 | INTRODUCTION

Nowadays, titanium is one kind of a very important structural metal. Titanium alloys possess high specific strength, excellent heat stability and strong corrosion resistance, and are widely applied in every field, such as the aerospace industry, automobile industry, biomedicine and so on.^{1,2} Nevertheless, titanium and titanium alloys can react with almost all kinds of refractory compounds (such as Al_2O_3 , MgO , etc) to produce brittle materials due to their high chemical activity under molten state, which results in a complex melting process and high cost to generate titanium alloys.^{3,4} To date, it is also a great challenge to choose a suitable crucible material for melting titanium and titanium alloys.

CaO may be a potential candidate for manufacturing crucible material to melt titanium and titanium alloys thanks to its high melting point and excellent thermodynamic properties. For instance, Sun et al have reported that TiNi alloy can be fabricated very well in CaO crucibles without pollution.⁵ Recently, the poor hydration resistance of CaO crucible in the air, which is a serious limitation for its industrial application, has also been improved enormously by Meng's group realized with rare-earth sesquioxide Y_2O_3 doping.⁶ More importantly, there is no reaction between $\text{CaO-Y}_2\text{O}_3$ and titanium alloys.

Besides crucible material, temperature is a very important physical parameter during the preparation process of titanium alloys. In the metallurgical industry, it is necessary to measure temperature with rapid speed and high precision. Optical thermometry may be a perfect choice to satisfy these requirements. Compared with conventional methods of temperature measurements, optical thermometry can realize a spatial distribution of temperature with sub-micrometer resolution. Meanwhile, optical thermometry also owns merits such as rapid response, non-contact, strong anti-jamming capability and so on.⁷⁻¹⁵ At present, the research hotspot about optical thermometry mainly focuses on fluorescence intensity ratio (FIR) technology utilizing pairs of thermally coupled energy levels in rare-earth ions.¹⁶⁻¹⁹ More specifically, the two thermally coupled energy levels used in FIR technology are closely separated, so the upper level can be populated from the lower level by a thermal excitation process at higher temperature.²⁰ In this case, the FIR of the two thermally coupled levels can be fitted well by Boltzmann equation and then the temperature measurement can be realized. There are a series of thermally coupled energy levels existing in rare-earth ions, such as Er^{3+} : $^2\text{H}_{11/2}/^4\text{S}_{3/2}$ levels, Tm^{3+} : $^3\text{F}_{2,3}/^3\text{H}_4$ levels, Eu^{3+} : $^5\text{D}_0/5\text{D}_1$ levels, etc.²¹⁻²⁷

In this paper, $\text{CaO-Y}_2\text{O}_3$: $\text{Yb}^{3+}/\text{Er}^{3+}$ were synthesized using a conventional high temperature solid state method. Yb^{3+} ions and Er^{3+} ions were selected as the sensitizers and activators respectively to use for temperature measurement, aimed at providing a real-time optical thermometry during the preparation process of titanium alloys. The optimal doping concentration of Yb^{3+} ions and Er^{3+} ions in $\text{CaO-Y}_2\text{O}_3$

have been explored. Meanwhile, the thermometry behaviors based on the Stark sublevels of Er^{3+} $^4\text{F}_{9/2}$ and $^4\text{I}_{13/2}$ have been studied in detail. In addition, since the raw materials Yb_2O_3 and Er_2O_3 possess similar physicochemical properties to Y_2O_3 , the doped Yb^{3+} ions and Er^{3+} ions in $\text{CaO-Y}_2\text{O}_3$ should have no effect on the application of manufacturing crucible material to melt titanium and titanium alloys. All the results reveal that $\text{CaO-Y}_2\text{O}_3$: $\text{Yb}^{3+}/\text{Er}^{3+}$ is a promising candidate that can realize an accurate optical thermometry.

2 | EXPERIMENTAL

2.1 | Chemicals

Y_2O_3 (99.99%), Yb_2O_3 (99.99%), and Er_2O_3 (99.99%) were purchased from Yangkou state-run rare-earth company. Analytical grade CaCO_3 was obtained from Chongqing Chuandong Chemical (Group) Co, Ltd. All of the oxides were used as raw materials without further treatment.

2.2 | Preparation

The $\text{CaO-Y}_2\text{O}_3$: $y\% \text{Yb}^{3+}/x\% \text{Er}^{3+}$ were synthesized using a conventional high temperature solid state method, specific as follows. Firstly, the raw materials were weighed in stoichiometric proportion. Secondly, they were mixed homogeneously for 30 minutes in an agate mortar and then the mixtures were put in a crucible. Finally, the powders were preheated in a furnace at 800°C for 3 hours, followed by further sintering at 1600°C for 5 hours to get the final samples. Here, it is necessary to note that the total concentration of Re^{3+} ions ($\text{Re}^{3+} = \text{Y}^{3+}, \text{Yb}^{3+}, \text{Er}^{3+}$) is 10%, which is relative to Ca^{2+} ions. Relative to Y^{3+} ions, the concentration of Yb^{3+} ions and Er^{3+} ions is $y\%$ and $x\%$ ($x = 0, 1, 2, 3, 4, 5, 6$; $y = 0, 1, 5, 10, 20, 30$), respectively.

2.3 | Characterization

A Persee XD-2 diffractometer supplied by Beijing Purkinje General Instrument Co., Ltd was used to record the powder X-ray diffraction (XRD) data. The spectral data were collected using a FLS920 spectrometer purchased from Edinburgh Instruments.

3 | RESULTS AND DISCUSSION

3.1 | Structure

The XRD patterns of $\text{CaO-Y}_2\text{O}_3$ and $\text{CaO-Y}_2\text{O}_3$: 10% $\text{Yb}^{3+}/4\% \text{Er}^{3+}$ are presented in Figure 1. Congruously,

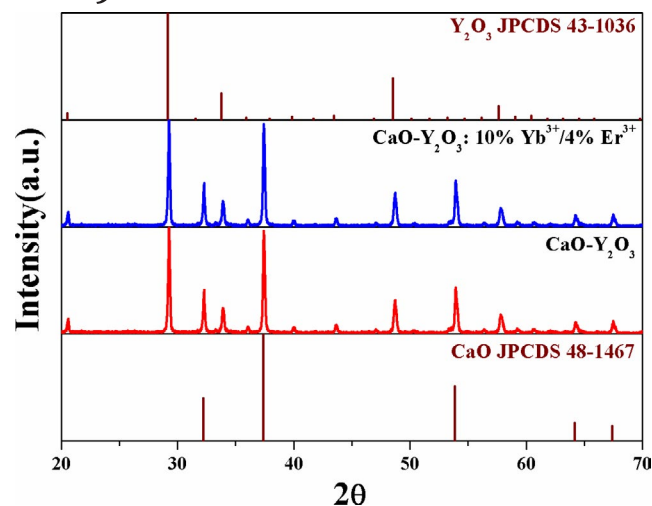


FIGURE 1 The X-ray diffraction (XRD) patterns of CaO-Y₂O₃ and CaO-Y₂O₃: 10% Yb³⁺/4% Er³⁺ with the standard XRD data of CaO (JCPDS 48-1467) and Y₂O₃ (JCPDS 43-1036)

the intensities and positions of the diffraction peaks for each sample match well with the standard cards of CaO (JCPDS 48-1467) and Y₂O₃ (JCPDS 43-1036), demonstrating the successful preparation of the target product without other impure phases. Moreover, the two samples show similar XRD patterns, indicating that Yb³⁺ and Er³⁺ are all incorporated into Y₂O₃ and formed a solid solution structure.

3.2 | Luminescence properties

3.2.1 | The UC properties of CaO-Y₂O₃: Yb³⁺/Er³⁺

In order to explore the optimal doping concentration of Yb³⁺ and Er³⁺ in CaO-Y₂O₃, samples doped with various Yb³⁺ and Er³⁺ concentrations were prepared and the corresponding UC spectra were also measured and are displayed in Figure 2A,B. Obviously, excited by 980 nm wavelength, two weak green emission bands and a strong red emission band exhibit in the range of 500-700 nm, which originate from ²H_{11/2} → ⁴I_{15/2} transition located at 522 nm, ⁴S_{3/2} → ⁴I_{15/2} transition located at 564 nm and ⁴F_{9/2} → ⁴I_{15/2} transition located at 661 nm of Er³⁺, respectively. Meanwhile, by fixing the doping concentration of Yb³⁺ and Er³⁺ respectively, the optimal doping concentrations of Yb³⁺ and Er³⁺ for the strongest UC emission were determined to be 10% and 4%. In addition, although the variable doping concentration of Yb³⁺ and Er³⁺ had no effect on the position of the three emission bands, the UC intensity dramatically changed. As depicted in Figure 2B, the red UC intensity is enhanced by a factor of 19, resulting from the efficient energy transfer (ET)

from sensitizer Yb³⁺ to activator Er³⁺. Figure 2C shows the near-infrared (NIR) emission spectra of CaO-Y₂O₃: 20% Yb³⁺/x % Er³⁺ excited by 980 nm wavelength. In this region, the spectra are composed of two bands, corresponding to the ²F_{5/2} → ²F_{7/2} transition located at 1028 nm of Yb³⁺ and ⁴I_{13/2} → ⁴I_{15/2} transition located at 1534 nm of Er³⁺. Clearly, the emission intensity of ²F_{5/2} → ²F_{7/2} transition of Yb³⁺ is reduced distinctly with the increase of Er³⁺ doping concentration, which is a direct proof for the efficient ET between the Yb³⁺ ions and Er³⁺ ions.

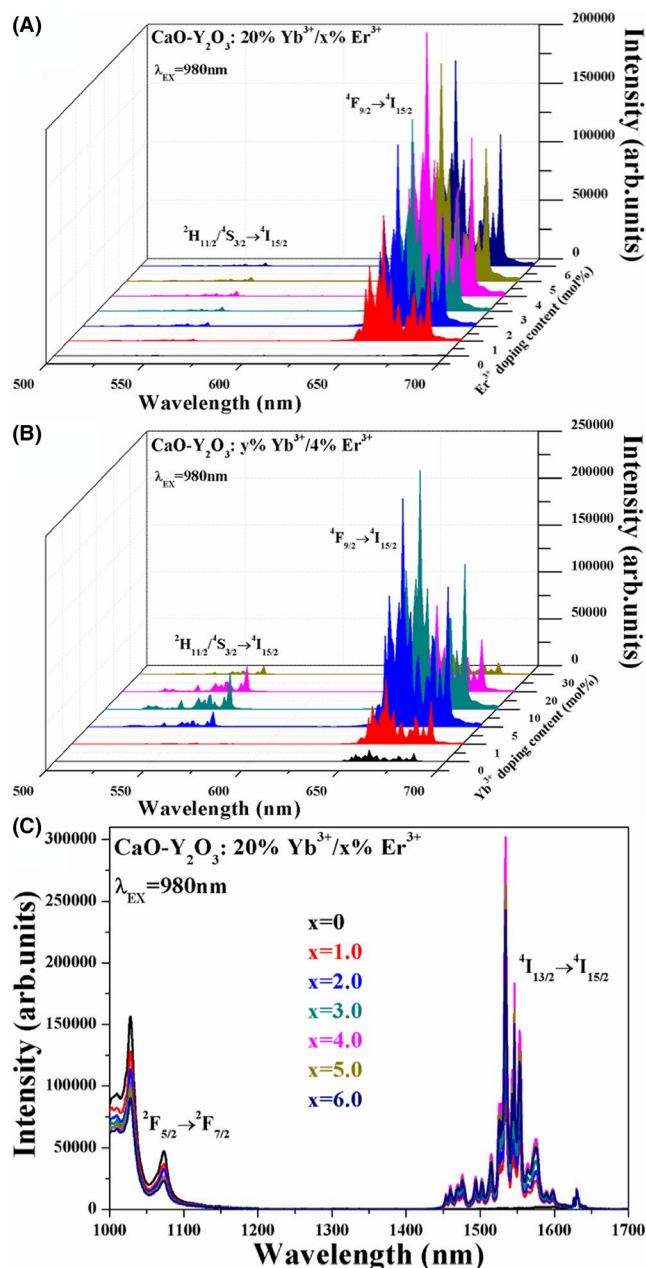


FIGURE 2 The UC spectra of (A) CaO-Y₂O₃: 20% Yb³⁺/x % Er³⁺ (x = 0, 1, 2, 3, 4, 5, 6) and (B) CaO-Y₂O₃: y % Yb³⁺/4% Er³⁺ (y = 0, 1, 5, 10, 20, 30). (C) The NIR spectra of CaO-Y₂O₃: 20% Yb³⁺/x % Er³⁺

FIGURE 3 A, Double logarithmic relationship of green and red UC emission versus excitation power in CaO-Y₂O₃: 10% Yb³⁺/4% Er³⁺. B, The energy level diagram with the related ET processes

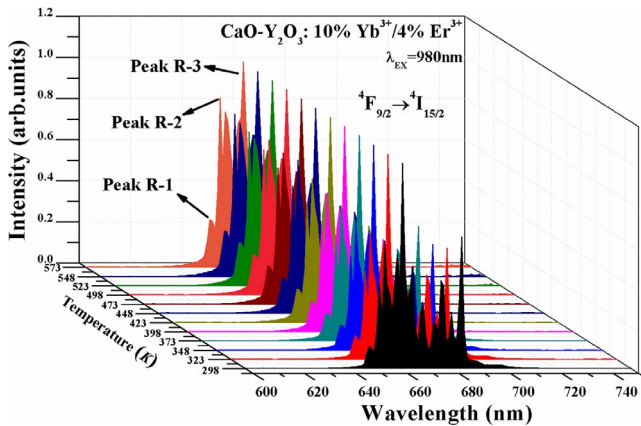
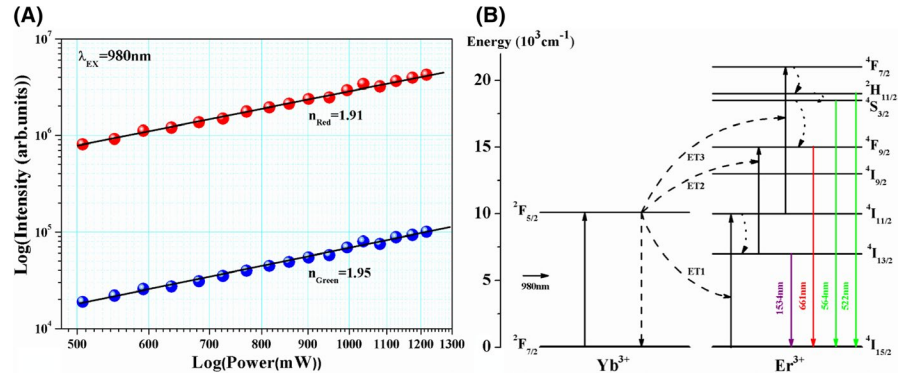


FIGURE 4 Temperature dependence of UC spectra in CaO-Y₂O₃: 10% Yb³⁺/4% Er³⁺ excited by 980 nm wavelength with low excitation power. The UC intensities of Peak R-3 are normalized

To further investigate the UC mechanism in CaO-Y₂O₃: Yb³⁺/Er³⁺, the dependence of the UC intensity on pump power was measured and is displayed in Figure 3A. The calculated slopes for green and red UC emissions are 1.91 and 1.95 respectively, revealing that both green and red UC emission are a two-photon process. Based on the above phenomenon, the energy level diagram of Yb³⁺ ions and Er³⁺ ions with the possible ET processes is schematically described in Figure 3B.^{28,29} Excited by 980 nm wavelength, Yb³⁺ ions at the ground state can be excited to ²F_{5/2} level by a ground state absorption process. Then Er³⁺ ions in the ground state can be populated to ⁴I_{11/2} level by receiving energy from the excited Yb³⁺ ions (ET1). Subsequently, the green emitting states ²H_{11/2}/⁴S_{3/2} of Er³⁺ ions can be populated by obtaining energy again from the excited Yb³⁺ ions (ET3) along with a multi-phonon relaxation (MPR) process. The Er³⁺ ions at ⁴I_{11/2} level can also be de-excited to ⁴I_{13/2} level by a MPR process. Then the red emitting state ⁴F_{9/2} of Er³⁺ ions can be populated through ET2 process. In addition, the MPR process from ⁴S_{3/2} of Er³⁺ ions is also a route for populating ⁴F_{9/2} level.

3.2.2 | The optical thermometry behaviors of CaO-Y₂O₃: Yb³⁺/Er³⁺

In most previous papers about UC optical thermometry, the thermally coupled levels ²H_{11/2} and ⁴S_{3/2} of Er³⁺ ions were the most commonly used due to the excellent UC properties and suitable energy gap. However, definitely, in this work, this pair of thermally coupled levels is hard to apply to temperature sensing because of the weak green UC emission. Actually, the thermally coupled red Stark sublevels of Er³⁺ ⁴F_{9/2} manifold can also be employed to measure the temperature with perfect sensitivity.^{30,31}

Subsequently, in order to investigate the temperature sensing behavior based on the thermally coupled red Stark sublevels, the thermal evolution red UC emission spectra of CaO-Y₂O₃: 10% Yb³⁺/4% Er³⁺ were measured and are shown in Figure 4. There are several emission peaks existing in the range of 600–700 nm, which belong to the Stark transitions of ⁴F_{9/2} → ⁴I_{15/2} transition. It is necessary to note that the emission intensities at 661 nm (named Peak R-3) have been normalized to 1. Intuitively, the intensities of almost all the peaks are increased relative to Peak R-3 with increasing temperature. That is to say, the variation rate of Peak R-3 is smaller than that of the other peaks, which makes it possible to measure the temperature by utilizing FIR between these red Stark sublevels. Here, Peak R-1 (located at 648 nm), Peak R-2 (located at 652 nm) and Peak R-3 were chosen as the targets for optical thermometry. The Boltzmann-type distribution law can be expressed as:

$$\text{FIR} = I_2/I_1 = B \exp(-\Delta E/k_B T), \quad (1)$$

with $B = g_1 v_1 \sigma_1 / g_2 v_2 \sigma_2$. Here, I_1 and I_2 are the integrated intensities of the lower level and the upper level, respectively. k_B and T define the Boltzmann constant and absolute temperature. The degeneracy degree, spontaneous emission, and absorption rate are symbolized as g , v and σ respectively. Based on Equation (1), the variation of FIR₁ between Peak R-1 and Peak R-3 with absolute temperature can be expressed as follows (see Figure 5A):

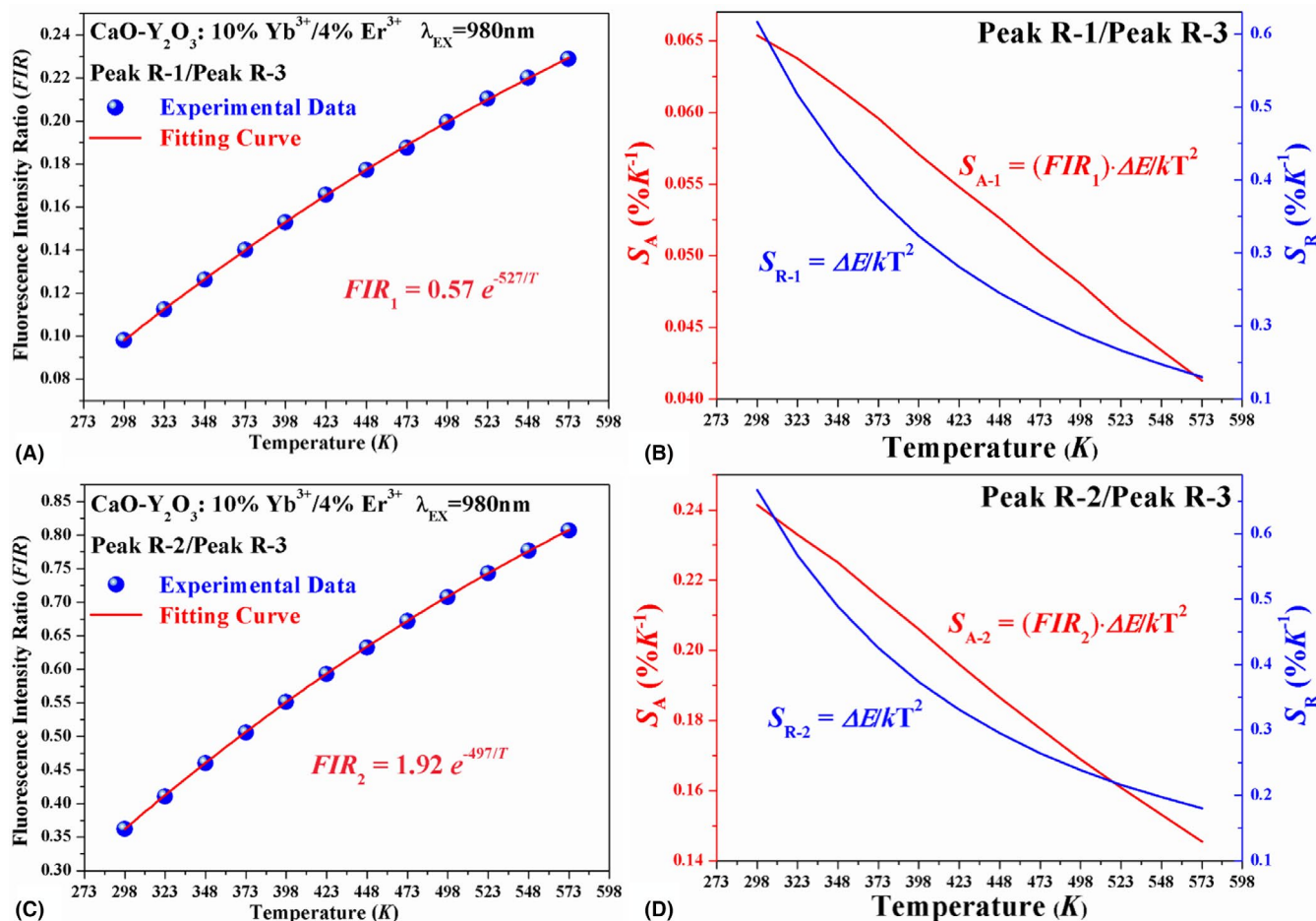


FIGURE 5 Temperature dependence of (A) FIR₁ between Peak R-1 and Peak R-3, (B) S_{A-1} and S_{R-1} , (C) FIR₂ between Peak R-2 and Peak R-3 and (D) S_{A-2} and S_{R-2} in $\text{CaO-Y}_2\text{O}_3: 10\% \text{Yb}^{3+}/4\% \text{Er}^{3+}$

$$\text{FIR}_1 = 0.57 \exp(-527/T), \quad (2)$$

Since $\Delta E/k_B = 527$, the calculated ΔE between Peak R-1 and Peak R-3 is approximately 366 cm^{-1} . Compared with the ΔE value obtained from the UC emission spectra (304 cm^{-1}), the error of ΔE is 62 cm^{-1} , resulting from the enhancement of the MPR and ET at high temperature.³² The absolute sensitivity S_A and relative sensitivity S_R , which are the vital parameters to evaluate the optical thermometry materials, can be calculated by the following expression:

$$S_A = |d(\text{FIR})/dT| = (\text{FIR}) \cdot (\Delta E/k_B T^2), \quad (3)$$

$$S_R = |d(\text{FIR})/(\text{FIR}) \cdot dT| = \Delta E/k_B T^2. \quad (4)$$

The corresponding values of sensor sensitivity as a function of temperature were calculated and are depicted in Figure 5B. The values of both S_A and S_R keep decreasing in the testing range from 298 to 573 K, which achieve the maximum $0.65 \times 10^{-3} \text{ K}^{-1}$ and $6.67 \times 10^{-3} \text{ K}^{-1}$ respectively at the beginning temperature. In addition, the FIR₂ between Peak R-2 and Peak R-3 can also be used to

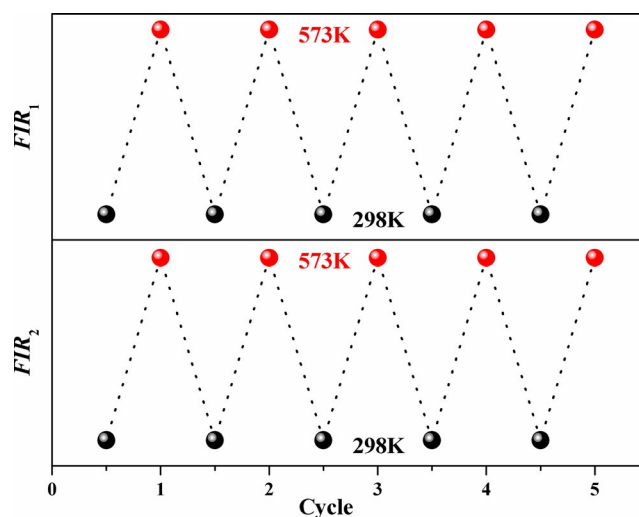


FIGURE 6 The repeatability study in the temperature cycling between 298 and 573 K

measure the temperature, which owns similar properties to FIR₁, as shown in Figure 5C,D. The repeatability study in the temperature cycling between 298 and 573 K for the

Stark transitions of $^4F_{9/2} \rightarrow ^4I_{15/2}$ transition is shown in Figure 6. The FIR_1 of Peak R-1 and Peak R-3 and FIR_2 of Peak R-2 and Peak R-3 were almost unchanged in the cycling process. It indicates the excellent repeatability and reliability of this material.

In order to evaluate the accuracy of optical thermometry in this work, two approaches were used to determine the temperature. To be specific, as shown in Figure 7A, a heating gun was used to heat the sample $\text{CaO-Y}_2\text{O}_3: 10\% \text{Yb}^{3+}/4\% \text{Er}^{3+}$ to a certain temperature and then the UC spectrum was collected

using a spectrometer at 980 nm wavelength excitation. At the same time, an infrared thermometer was also utilized as a contrast to record the temperature. The temperature calculated by FIR_1 and FIR_2 as well as the data recorded by the infrared thermometer are all plotted in Figure 7B. Fortunately, the values of temperature whether deduced by FIR_1 or FIR_2 match well with the data recorded by the infrared thermometer, demonstrating the high accuracy of $\text{CaO-Y}_2\text{O}_3: 10\% \text{Yb}^{3+}/4\% \text{Er}^{3+}$ for optical thermometry. The maximum absolute error for FIR_1 and FIR_2 is 3.1 and 3.2 K, respectively.

FIGURE 7 A, Scheme of the setup for the temperature determination experiment. B, The temperature calculated by FIR_1 and FIR_2 as well as detected using an infrared thermometer. Inset, the red UC spectra with normalized intensity measured at 298 and 433 K

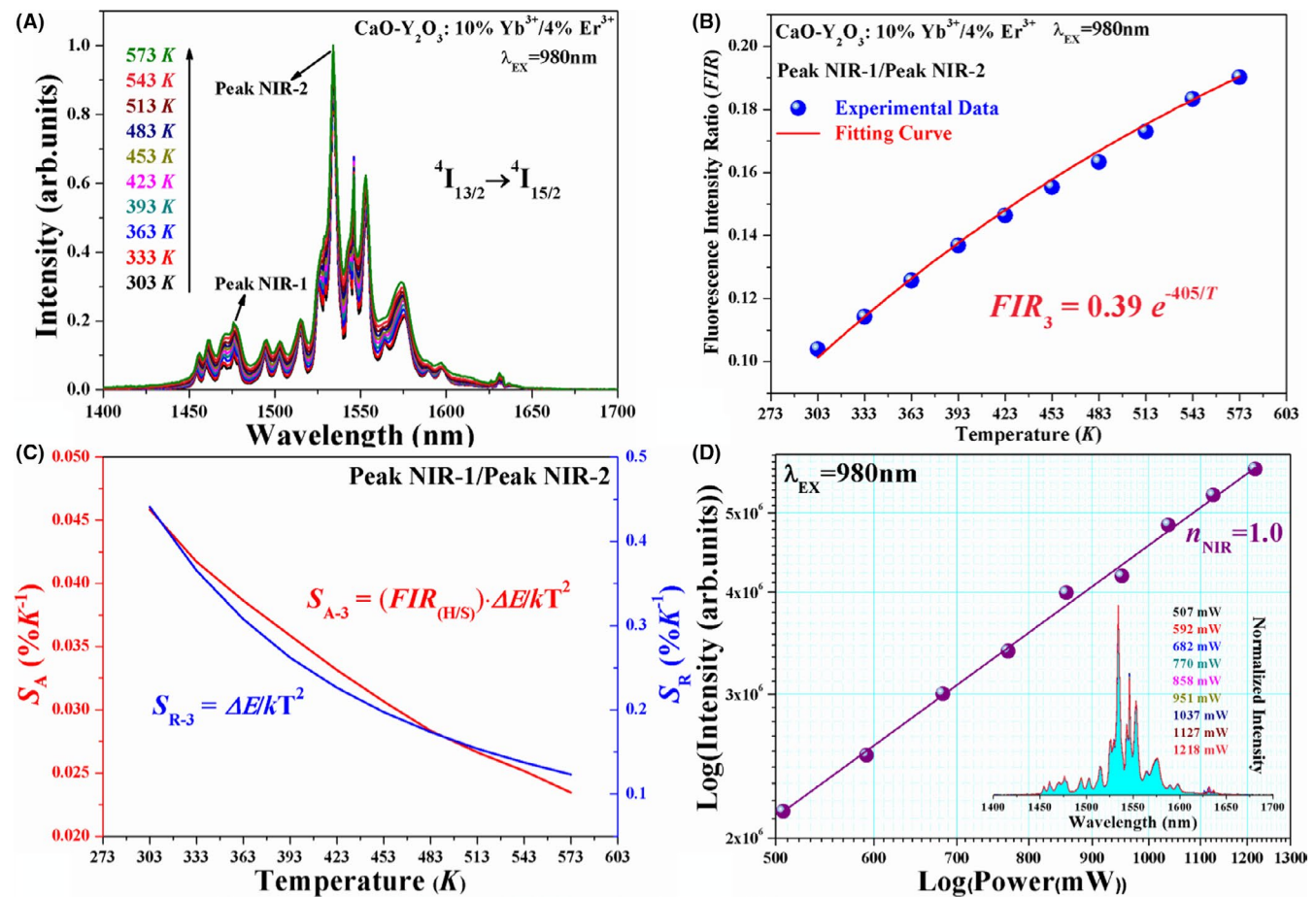
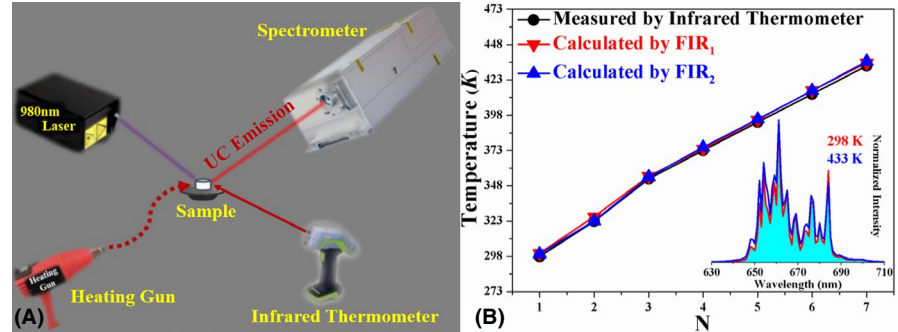


FIGURE 8 Temperature dependence of (A) $^4I_{13/2} \rightarrow ^4I_{15/2}$ transition, (B) FIR_3 between Peak NIR-1 and Peak NIR-2 and (C) the corresponding S_{A-3} and S_{R-3} . (D) Double logarithmic relationship of $^4I_{13/2} \rightarrow ^4I_{15/2}$ transition versus excitation power. Inset, the corresponding NIR spectra with normalized intensity excited by various pump power

Beyond that, the relationship of $^4I_{13/2} \rightarrow ^4I_{15/2}$ transition versus temperature in $\text{CaO-Y}_2\text{O}_3$: 10% Yb^{3+} /4% Er^{3+} has also been explored. As illustrated in Figure 8A, several emission peaks exist in the range of 1400–1700 nm, originating from the Stark transitions of $^4I_{13/2} \rightarrow ^4I_{15/2}$ transition. The intensities of Peak NIR-2 (at 1534 nm) have been normalized to 1. The relative intensities of the other peaks change regularly with the rising temperature. Here, Peak NIR-1 (at 1476 nm) and Peak NIR-2, which derive from a pair of the thermally coupled Stark sublevels with a small energy separation between them ($\Delta E = 256 \text{ cm}^{-1}$, calculated from the emission spectra), were chosen as targets for optical thermometry. Based on the Boltzmann-type distribution law, the variation of FIR_3 between Peak NIR-1 and Peak NIR-2 with absolute temperature can be written as follows (see Figure 8B).

$$\text{FIR}_3 = 0.39 \exp(-405/T), \quad (5)$$

According to the above fitting equation, the calculated ΔE between Peak NIR-1 and Peak NIR-2 is approximately 281 cm^{-1} , which is similar to the value obtained from the NIR emission spectra. The corresponding S_{A-3} and S_{R-3} are also calculated and are depicted in Figure 8C. The values of S_{A-3} and S_{R-3} keep decreasing in the testing range with the maximum $0.46 \times 10^{-3} \text{ K}^{-1}$ and $4.41 \times 10^{-3} \text{ K}^{-1}$ respectively at the beginning temperature.

Generally, in order to ensure the high sensitivity of UC optical thermometry, the excitation power should be low enough to avoid the laser-induced thermal effect.^{32–34} Actually, the negative impact of this thermal effect mainly occurs in the multi-photon UC process with little influence on a one-photon luminescence process.³⁵ Figure 8D shows the dependence of $^4I_{13/2} \rightarrow ^4I_{15/2}$ transition on pump power of 980 nm excitation wavelength, indicating a one-photon process for $^4I_{13/2} \rightarrow ^4I_{15/2}$ transition. Meanwhile, as observed from the illustration in Figure 8D, the relative intensity of every Stark transition almost has no change with increasing pump power, which means that a high excitation pump power can be used to obtain strong NIR emission and a good signal-to-noise ratio for optical thermometry without the influence of the laser-induced thermal effect.

Indeed, the purpose of this work was to provide a real-time optical thermometry during the preparation process of titanium alloys realized using FIR technology. However, restricted by the condition of characterization, the highest testing temperature for optical thermometry in this work is only about 600 K, which is far below the melting temperature $\sim 1800 \text{ K}$ of titanium alloys. At present, the highest testing temperature for optical thermometry reported in the previous literature is approximately 1000 K, which is also restricted by the condition of characterization.³⁶ Nevertheless, we believe that $\text{CaO-Y}_2\text{O}_3$: $\text{Yb}^{3+}/\text{Er}^{3+}$ would own excellent temperature sensing performance at high temperatures because of its good thermodynamic property and strong UC emission.

4 | CONCLUSIONS

In summary, the optical thermometry behaviors of $\text{CaO-Y}_2\text{O}_3$: $\text{Yb}^{3+}/\text{Er}^{3+}$ based on the Stark sublevels of $\text{Er}^{3+} ^4F_{9/2}$ and $^4I_{13/2}$ have been investigated in detail. The results reveal that a high measurement precision can be obtained by utilizing the Stark sublevels of $\text{Er}^{3+} ^4F_{9/2}$ to measure the temperature with a maximum absolute error of only about 3 K. Besides that, we found that the laser-induced thermal effect has almost no influence on the temperature measurement conducted by using the FIR of the Stark sublevels of $\text{Er}^{3+} ^4I_{13/2}$, which means that a high excitation pump power can be used to obtain strong NIR emission and good signal-to-noise ratio for optical thermometry. Briefly, it can be proposed that $\text{CaO-Y}_2\text{O}_3$: $\text{Yb}^{3+}/\text{Er}^{3+}$ is an excellent temperature sensing material with high measurement precision.


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