

Excellent optical thermometry based on short-wavelength upconversion emissions in $\text{Er}^{3+}/\text{Yb}^{3+}$ codoped CaWO_4

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Received September 6, 2012; revised October 9, 2012; accepted October 17, 2012;
posted October 17, 2012 (Doc. ID 175753); published November 22, 2012

Excited by a 980 nm laser, upconversion emissions centered at 384 ($\text{Er}^{3+}:^4\text{G}_{11/2} \rightarrow ^4\text{I}_{15/2}$) and 408 nm ($\text{Er}^{3+}:^2\text{H}_{9/2} \rightarrow ^4\text{I}_{15/2}$) in $\text{Er}^{3+}/\text{Yb}^{3+}$ codoped polycrystalline CaWO_4 were successfully obtained. The $^4\text{G}_{11/2}$ and $^2\text{H}_{9/2}$ states of Er^{3+} were verified to be thermally coupled levels, which can emit the shortest wavelength emissions for optical thermometry known so far. Based on the change of their intensity ratio with temperature, an excellent optical thermometer can be designed, which can provide accurate temperature measurement from room temperature up to 873 K. More importantly, the sensitivity achieved here is much higher than reported temperature sensors based on Er^{3+} green luminescence. © 2012 Optical Society of America

OCIS codes: 190.7220, 160.4760, 300.2140, 280.4788.

By providing a noncontact temperature measurement through probing the temperature dependent fluorescence, optical temperature sensing devices, based on luminescent materials with rare earth (RE) ions as the activators, have attracted much interest in recent years [1]. Research in this field has been significantly stimulated by the demand for noncontact, safe, inexpensive, and reliable sensors in the monitoring of electrical transformer temperature in power stations, oil refineries, coal mines, and building fire detectors, where the contacting thermometry technique cannot be used.

As an optical thermometry method, the fluorescence intensity ratio (FIR) technique based on the measurement of luminescence intensities from two thermally coupled levels (TCL) of one kind of RE ion is independent of spectrum losses and fluctuations in the excitation intensity, so it can provide more accurate temperature measurements. Presently, optical temperature sensors in the low and medium temperature range have been developed based on materials using Er^{3+} as the activator, which provides green upconversion (UC) emissions from the thermally coupled $^2\text{H}_{11/2}$ and $^4\text{S}_{3/2}$ states under a compact and cost-effective continuous wave near infrared diode laser excitation [2–6]. However, the drawback of these sensors is that the green emission bands of Er^{3+} are all overlapping to some extent [2–6]. Band overlapping would cause the measured FIR to deviate from their real values, consequently resulting in larger detection error [1]. Furthermore, in order to extend the optical thermometry into the high temperature range, shorter wavelength emissions should be utilized because they can effectively avoid the influence of the black-body radiation generated by the detected object. Considering these aspects, it is of technological importance and scientifically interesting to explore more appropriate TCL.

Through the energy level diagram of Er^{3+} ions, it is noted that the energy gap ΔE between the $^4\text{G}_{11/2}$ and $^2\text{H}_{9/2}$ states is about 1530 cm^{-1} , satisfying the requirement for the TCL ($200 \leq \Delta E \leq 2000\text{ cm}^{-1}$) [1]. More importantly, the emissions due to transitions from the two

coupled states to the ground state are in the ultraviolet region and are well separated due to the relatively large ΔE [7]. Therefore, it is feasible to use these two coupled states for temperature measurement to resolve existing problems in optical thermometry as mentioned above. However, the emissions from the $\text{Er}^{3+}:^4\text{G}_{11/2}$ and $^2\text{H}_{9/2}$ states were mainly observed in fluorides [7]. For stability reasons, it is important to choose an appropriate oxide host material for thermometry.

In this Letter, polycrystalline CaWO_4 was selected as the host material due to its good chemical and physical stability and low phonon threshold energy. The $^4\text{G}_{11/2}$ and $^2\text{H}_{9/2}$ states of Er^{3+} were verified to be TCL. By using the 384 and 408 nm emissions from this TCL, $\text{Er}^{3+}/\text{Yb}^{3+}$ codoped CaWO_4 showed great potential for optical temperature sensor with several advantages over the existing Er^{3+} green fluorescence based sensors.

The $\text{Er}^{3+}/\text{Yb}^{3+}$ codoped polycrystalline CaWO_4 was synthesized by a high temperature solid-state reaction. The sample is prepared with the following starting composition ratios (in mol. %): $50\text{CaCO}_3\text{-}50\text{WO}_3\text{-}0.15\text{Er}_2\text{O}_3\text{-}2.5\text{Yb}_2\text{O}_3$. The detailed preparation process is similar to our previous work [8]. X-ray diffraction analysis revealed that the sample has the Scheelite-type tetragonal structure, and all diffraction peaks can be indexed by the standard powder diffraction file card no. 77-2236. The temperature dependence of UC luminescence spectra was obtained by using the experimental setup described in our previous work [9]. The sample temperature was increased from 303 to 873 K.

Figure 1 shows the UC emission spectra of the sample under a 980 nm diode laser excitation with the pumping power of 100 mW. The sample exhibits very bright green luminescence originating from the $^2\text{H}_{11/2}$ and $^4\text{S}_{3/2}$ levels of Er^{3+} ions. Relatively intense 384 and 408 nm short-wavelength UC emissions respectively attributed to the $^4\text{G}_{11/2} \rightarrow ^4\text{I}_{15/2}$ and $^2\text{H}_{9/2} \rightarrow ^4\text{I}_{15/2}$ transitions of Er^{3+} ions are obtained. We also studied the UC emissions from the $\text{Er}^{3+}/\text{Yb}^{3+}$ codoped Y_2O_3 , Gd_2O_3 , and ZrO_2 phosphors under a 980 nm laser excitation and found that the

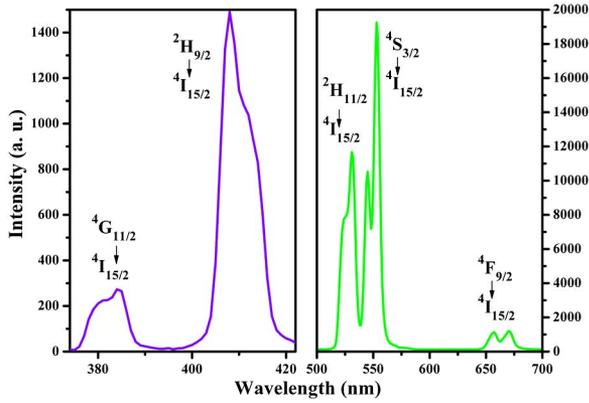


Fig. 1. (Color online) UC emission spectra of $\text{Er}^{3+}/\text{Yb}^{3+}$ codoped polycrystalline CaWO_4 under 980 nm laser excitation with the power of 100 mW.

$\text{Er}^{3+}/\text{Yb}^{3+}$ codoped CaWO_4 has excellent ultraviolet and visible UC emissions even excited with a lower pumping power. This is mainly due to the relatively low phonon threshold energy for CaWO_4 (807 cm^{-1}) and less OH^{-1} groups owing to the high-temperature solid-state reaction method used here [8].

The inset of Fig. 2 shows the log–log plots of intensity I for 384 and 408 nm emissions as a function of pumping power P . For an unsaturated UC process, I and P follow the relationship of $I \propto P^n$, where n is the number of the pumping photons required to excite RE ions from the ground state to the excited state. It can be seen that the values of n are 2.84 ± 0.04 and 2.78 ± 0.05 for the ${}^4\text{G}_{11/2} \rightarrow {}^4\text{I}_{15/2}$ and ${}^2\text{H}_{9/2} \rightarrow {}^4\text{I}_{15/2}$ transitions, respectively. This result demonstrates that the three-photon process has been involved in the above transitions. Figure 2 shows the proposed mechanisms to explain the short-wavelength UC emissions (GSA denotes ground state absorption; ESA denotes excited state absorption). Under a 980 nm laser excitation, the emitting states of Er^{3+} are populated not only by GSA and ESA processes but also by the efficient energy transfer from Yb^{3+} to Er^{3+} , and the latter is dominant. In addition, some cross-relaxation processes may also be involved [10].

To verify that the ${}^4\text{G}_{11/2}$ and ${}^2\text{H}_{9/2}$ are thermally coupled, the 384 and 408 nm UC emissions were studied

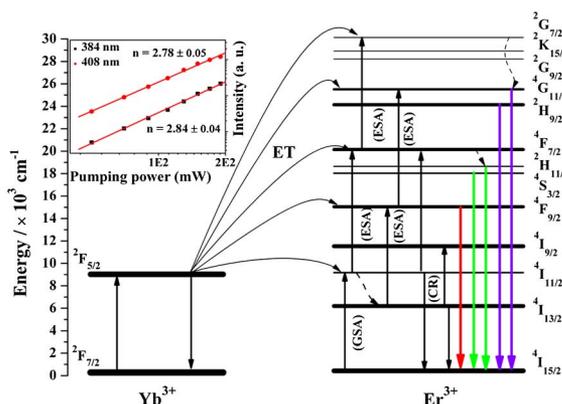


Fig. 2. (Color online) Energy level diagram of Er^{3+} and Yb^{3+} as well as the proposed UC mechanisms; inset figure shows the log–log plots of UC emission intensity as a function of a 980 nm laser pumping power.

as a function of temperature ranging from 303 to 873 K. Figure 3(a) shows the corresponding emission spectra for the sample at 303 and 873 K, and the power of the 980 nm laser was set at 150 mW. To clearly observe the relative change in the spectra, the emission intensity has been normalized. In fact, a 1.8-fold enhancement has been achieved for the 384 nm emission at 543 K compared with that at 303 K, and the 408 nm emission gradually decreases as the temperature increases. But both emissions still show a high signal to noise ratio even at 873 K. It can be seen from Fig. 3(a) that the position of the emission bands hardly changes with the increase of temperature, but the intensity ratio between 384 and 408 nm luminescence obviously varies. The change in the ratio is attributed to the corresponding energy gap between the ${}^2\text{H}_{9/2}$ and ${}^4\text{G}_{11/2}$ levels, which allows the ions on ${}^2\text{H}_{9/2}$ state to be thermally populated onto the ${}^4\text{G}_{11/2}$ state with the increase of temperature. According to the theory by Wade *et al.* [1], the FIR from the TCL of RE ions is modified as

$$\text{FIR} \equiv I_i/I_j = A \exp(-\Delta E/k_B T) + B, \quad (1)$$

where I_i and I_j are intensities of emissions from the upper and the lower TCL, A is a constant, B is the offset factor, ΔE is the energy difference between TCL, k_B is the Boltzmann constant, and T is the absolute temperature. Figure 3(b) presents the FIR between 384 and 480 nm emissions as a function of temperature in the range of 303–873 K. The experimental data are fitted by Eq. (1). It can be observed that the fittings agree well with the experimental data. A and B are fitted to be 28.55 and 0.11, respectively, and ΔE is fitted to be 1455 cm^{-1} , close to the value calculated from the emission spectra (1530 cm^{-1}). These results confirmed that the ${}^4\text{G}_{11/2}$ and ${}^2\text{H}_{9/2}$ states are TCL. Several temperature cycles have been tested and good reproducibility was obtained.

For optical thermometry, it is of great importance to understand the rate of change in the FIR in response to the variation of temperature. This value is known as the sensitivity. To allow the comparison between the sensitivities obtained from different TCL, the absolute sensitivity S_a is defined as [1]

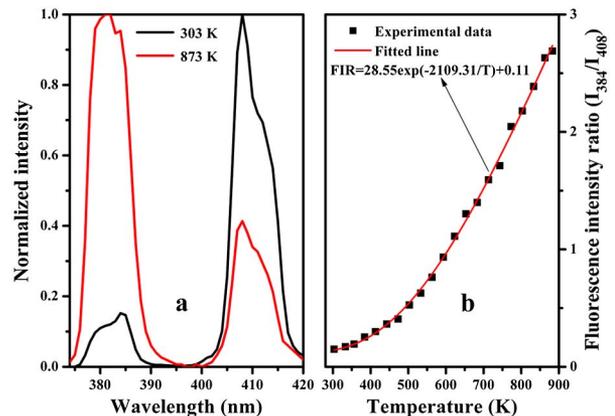


Fig. 3. (Color online) (a) The normalized short-wavelength UC emission spectra at 303 and 873 K and (b) FIR between the 384 and 408 nm emissions as a function of temperature in the range of 303–873 K.

Table 1. Sensitivities of Optical Temperature Sensors Based on the Short-Wavelength and the Green UC Fluorescence of Materials with Er³⁺ as Activator

Sensing Materials	Transitions	S_a (K ⁻¹)	Temperature Range (K)	Reference
CaWO ₄	⁴ G _{11/2} , ² H _{9/2} → ⁴ I _{15/2}	2109/T ²	303–873	This work
ZnO	² H _{11/2} , ⁴ S _{3/2} → ⁴ I _{15/2}	880/T ²	273–573	[2]
Chalcogenide glass	² H _{11/2} , ⁴ S _{3/2} → ⁴ I _{15/2}	928/T ²	293–498	[3]
Fluorotellurite glass	² H _{11/2} , ⁴ S _{3/2} → ⁴ I _{15/2}	1036/T ²	299–543	[4]
Y ₂ SiO ₅	² H _{11/2} , ⁴ S _{3/2} → ⁴ I _{15/2}	817/T ²	300–600	[5]
BaTiO ₃	² H _{11/2} , ⁴ S _{3/2} → ⁴ I _{15/2}	940/T ²	322–466	[6]

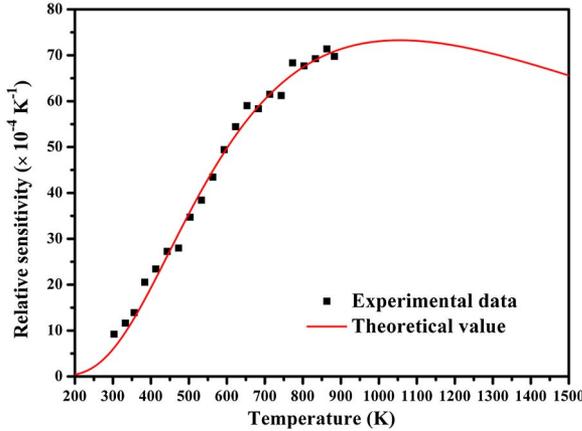


Fig. 4. (Color online) Calculated relative sensitivity (curve) and the measured values (squares) for the sample at temperatures from 303 to 873 K.

$$S_a \equiv \Delta E/k_B T^2. \quad (2)$$

Equation (2) suggests that using pairs of levels with larger energy differences are in favor of higher sensitivity. Table 1 shows the expression of the sensitivity in this work. For comparison, the sensitivities for sensors based on the green emissions of Er³⁺ are also presented. It was found that the sensitivity achieved here is the largest among all sensors. This result is attributed to the much larger energy gap between ⁴G_{11/2} and ²H_{9/2} states, which is also in favor of much higher resolution.

Considering practical applications, it is necessary to know the variation of sensitivity with temperature. For this purpose, the relative sensitivity S_r has been defined as [2,3]

$$S_r \equiv \text{FIR} \times \Delta E/k_B T^2. \quad (3)$$

Figure 4 presents the S_r as a function of temperature. It can be seen that the sensitivity keeps increasing in our experimental temperature range and reaches the maximum value 0.0073 K⁻¹, which is lower than the highest value so far and recently reported by us [8]. But those reported sensitivities at higher temperatures become much worse [2–6,8]. Additionally, the measurement error, which is a significant factor for judging a temperature sensor, can be estimated from the relative sensitivity using the following equation [11]:

$$\Delta T = \Delta \text{FIR} \times k_B T^2 / \text{FIR} \times \Delta E. \quad (4)$$

A practical optical temperature-sensing device requires a simple and inexpensive electronic circuit to process the ratio between the two light signals. Although the absolute sensitivity based on Tm³⁺ emissions is the highest so far [9], the corresponding S_r is much lower than that in this work. Therefore, when employing a signal division circuitry with the same precision, a much smaller error can be expected by using the 384 and 408 nm emissions from Er³⁺/Yb³⁺ codoped CaWO₄ phosphor due to the larger values of S_r . Meanwhile, the well separated 384 and 408 nm emissions in the ultraviolet region can avoid the interference of background radiation. Therefore, the coupled short-wavelength emissions of Er³⁺ is more suitable to be applied in high temperature measurement and can also guarantee better accuracy.

In conclusion, an optical temperature sensor based on the shortest wavelength emissions to date was developed. The result revealed that thermometry based on the 384 and 408 nm emissions from the Er³⁺/Yb³⁺ codoped CaWO₄ phosphor is more superior to those based on the Er³⁺ green emissions.

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