

## Optical Thermometry through Green Upconversion Emissions in Er<sup>3+</sup>/Yb<sup>3+</sup>-Codoped CaWO<sub>4</sub> Phosphor

Wei Xu, Xiaoyang Gao<sup>1</sup>, Longjiang Zheng<sup>1</sup>, Peng Wang, Zhiguo Zhang\*, and Wenwu Cao<sup>2</sup>

Condensed Mater Science and Technology Institute, Harbin Institute of Technology, Harbin 150001, China

<sup>1</sup>Institute of Electrical Engineering, Yanshan University, Qinhuangdao 66004, China

<sup>2</sup>Materials Research Institute, The Pennsylvania State University, University Park, PA 16802, U.S.A.

Received April 10, 2012; accepted May 30, 2012; published online June 18, 2012

Under 980 nm excitation, the temperature-dependent green upconversion emissions from Er<sup>3+</sup>/Yb<sup>3+</sup>-codoped CaWO<sub>4</sub> phosphor were studied at temperatures from 294 to 923 K. By using the fluorescence intensity ratio technique, the maximum sensitivity for temperature measurement achieved here is approximately 0.0092 K<sup>-1</sup>, which is much higher than previously reported temperature sensors based on the fluorescence of Er<sup>3+</sup> ions in other host materials. With the efficient upconversion fluorescence, the Er<sup>3+</sup>/Yb<sup>3+</sup>-codoped CaWO<sub>4</sub> is a very promising candidate for optical high-temperature sensors with high sensitivity and good accuracy. © 2012 The Japan Society of Applied Physics

Optical temperature sensors based on the fluorescence intensity ratio (FIR) technique have recently attracted considerable attention for their high sensitivity and accuracy.<sup>1,2)</sup> The FIR technique commonly uses rare-earth (RE) ion-doped materials as the sensing medium, the fluorescence being induced by a range of widely available excitation sources and detected via a straightforward procedure. Through the comparison of fluorescence intensities from two thermally coupled levels of RE ions, the temperature can be measured at a distance from the object. Therefore, the fluorescence-based temperature sensors are particularly advantageous for operating in electromagnetically and/or thermally harsh environments.

Green upconversion (UC) emissions from Er<sup>3+</sup> ions (<sup>2</sup>H<sub>11/2</sub> and <sup>4</sup>S<sub>3/2</sub> thermally coupled levels) are especially appropriate for optical thermometry. Yb<sup>3+</sup> is usually used as the preferred sensitizer due to its large absorption cross section at 980 nm and efficient energy transfer from Yb<sup>3+</sup> to Er<sup>3+</sup>. Some successful applications on the FIR technique using green UC emissions of Er<sup>3+</sup> have been performed and the host materials are mainly glass matrices.<sup>3–8)</sup> The Er<sup>3+</sup>-doped fluoride glass possesses high efficiency and low excitation power, however, the maximum operating temperature is below 500 K.<sup>5,7)</sup> Although the Er<sup>3+</sup>-doped silica increases the measured temperature up to 873 K,<sup>8)</sup> the much lower fluorescence efficiency limits the application in optical thermometry. Thus, it is of technological and scientific importance to look for an appropriate host matrix with higher fluorescence efficiency and higher operating temperature for optical temperature sensors.

Calcium tungstate (CaWO<sub>4</sub>) has been thought to be one of the potential luminescent materials owing to its outstanding properties, including good chemical and physical stability, high density and reflection coefficient, as well as low phonon threshold energy.<sup>9–11)</sup> It is expected that CaWO<sub>4</sub> could be an appropriate host for optical thermometry applications. In this work, we preliminarily investigated the characteristics of Er<sup>3+</sup>/Yb<sup>3+</sup>-codoped CaWO<sub>4</sub> phosphor for use in optical temperature sensors, and various advantages over the existing Er<sup>3+</sup>-fluorescence-based sensors have been achieved.

The Er<sup>3+</sup>/Yb<sup>3+</sup>-codoped CaWO<sub>4</sub> phosphor was prepared by using the high-temperature solid-state reaction method.

CaCO<sub>3</sub> and WO<sub>3</sub> were mixed at a 1 : 1 molar ratio, and 0.05 mol % Er<sub>2</sub>O<sub>3</sub> and 0.5 mol % Yb<sub>2</sub>O<sub>3</sub> were added. The starting materials were fully mixed and grinded for 3 h. The powder was subsequently placed in a corundum crucible and sintered in a furnace for 10 h at 1300 °C. The Er<sup>3+</sup>/Yb<sup>3+</sup>-codoped CaWO<sub>4</sub> phosphor was finally pressed into a thin disk with a diameter of 1.3 cm. The crystal phase was confirmed by X-ray diffraction (XRD) method with a powder diffractometer (Rigaku DMAX2500) using Cu K $\alpha$  radiation ( $\lambda = 0.154$  nm). The Fourier transform infrared (FT-IR) spectroscopy was measured by a Perkin-Elmer 2000 FT-IR spectrophotometer in the range of 400–7000 cm<sup>-1</sup> using KBr pellets. To investigate the temperature-dependent UC luminescence, the sample was placed in a mini furnace and its temperature was increased from 294 to 923 K (the highest temperature of the furnace). The temperature of the sample was monitored using a copper–constantan thermocouple and controlled with a proportional-integral-derivative loop feedback temperature control system. The UC emission spectra were recorded using an Ocean Optics QE65000 fiber spectrometer with a resolution of less than 1 nm. A 980 nm diode laser was used as the pumping source with an excitation power of 230 mW. The laser beam was not focused through a lens, and its corresponding power density on the sample is about 4.13 W/cm<sup>2</sup>.

Figure 1 presents the XRD patterns of the Er<sup>3+</sup>/Yb<sup>3+</sup>-codoped CaWO<sub>4</sub> phosphor and the data from the PDF card as a reference pattern with tetragonal structure. It can be seen that the sample has Scheelite-type tetragonal structures. The sharp diffraction peaks suggest that the sample was well crystallized. Figure 2 shows the green UC emission spectra of the Er<sup>3+</sup>/Yb<sup>3+</sup>-codoped CaWO<sub>4</sub> phosphor at 294 and 923 K. The spectra exhibit two main emission bands centered at 530 and 552 nm. The widely accepted UC mechanisms are illustrated in the inset of Fig. 2 (GSA denotes ground state absorption; ESA denotes excited state absorption). Under a 980 nm laser excitation, the <sup>4</sup>I<sub>11/2</sub> and <sup>4</sup>F<sub>7/2</sub> states of Er<sup>3+</sup> are populated not only by GSA and ESA processes but also by the energy transfer (ET) from Yb<sup>3+</sup> to Er<sup>3+</sup>, and the latter is dominant.<sup>12)</sup> The <sup>2</sup>H<sub>11/2</sub> and <sup>4</sup>S<sub>3/2</sub> levels are subsequently populated by the nonradiative relaxation from the <sup>4</sup>F<sub>7/2</sub> level. Finally, emissions at 530 and 552 nm are produced by the <sup>2</sup>H<sub>11/2</sub> → <sup>4</sup>I<sub>15/2</sub> and <sup>4</sup>S<sub>3/2</sub> → <sup>4</sup>I<sub>15/2</sub> transitions, respectively. It can be seen from Fig. 2 that the positions of the emission bands barely change with the

\*E-mail address: zhangzhiguo@hit.edu.cn

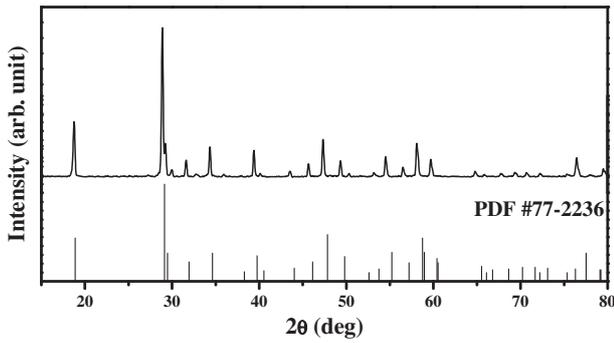


Fig. 1. XRD patterns of the Er<sup>3+</sup>/Yb<sup>3+</sup>-codoped CaWO<sub>4</sub> phosphor.

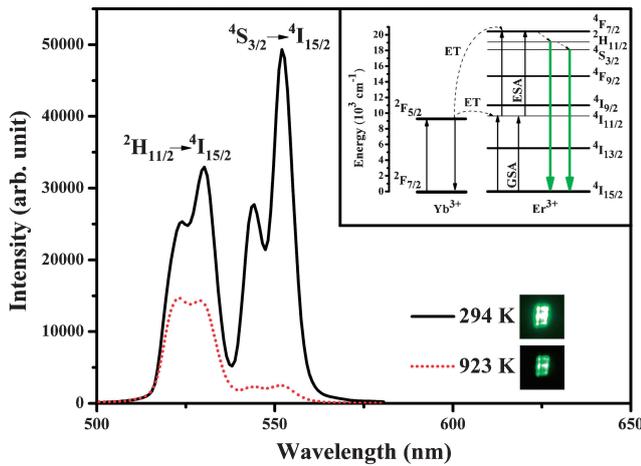


Fig. 2. Green upconversion emissions at 294 and 923 K under 980 nm excitation with the power density of 4.13 W/cm<sup>2</sup>; the insets show the corresponding photographs and mechanisms for generating the green upconversion emissions in the Er<sup>3+</sup>/Yb<sup>3+</sup>-codoped system.

increase of temperature, but the intensity ratio between 530 and 552 nm luminescence obviously varies with temperature. The change in the ratio is attributed to the small energy gap between the <sup>2</sup>H<sub>11/2</sub> and <sup>4</sup>S<sub>3/2</sub> levels (about 750 cm<sup>-1</sup> from the emission spectra), which allows the ions on <sup>4</sup>S<sub>3/2</sub> to be thermally populated onto the <sup>2</sup>H<sub>11/2</sub> state with the increase of temperature. The relative population for the thermally coupled levels is known to follow the Boltzmann-type distribution, and the intensity ratio *R* of the fluorescence from <sup>2</sup>H<sub>11/2</sub> and <sup>4</sup>S<sub>3/2</sub> levels is given by<sup>1)</sup>

$$R \equiv \frac{I_{530}}{I_{552}} = \frac{A_{HG}g_H\sigma_H w_H}{A_{SG}g_S\sigma_S w_S} \exp\left(-\frac{\Delta E}{k_B T}\right) = C \exp\left(-\frac{\Delta E}{k_B T}\right), \quad (1)$$

where *A* and *g* are the radiative transition rate and degeneracy for <sup>2</sup>H<sub>11/2</sub> and <sup>4</sup>S<sub>3/2</sub> levels of Er<sup>3+</sup> ions, respectively;  $\sigma$  is the response of the detection system at the emission angular frequency *w*;  $\Delta E$  is the energy gap between <sup>2</sup>H<sub>11/2</sub> and <sup>4</sup>S<sub>3/2</sub> levels; *k<sub>B</sub>* is Boltzmann constant; *T* is the absolute temperature, and the preexponential constant is given as  $C = A_{HG}g_H\sigma_H w_H / A_{SG}g_S\sigma_S w_S$ . Figure 3(a) shows the monolog plot of the FIR of Er<sup>3+</sup> green UC emissions at 530 and 552 nm as a function of inverse absolute temperature in the range of 294–923 K. The experimental data are well fitted to

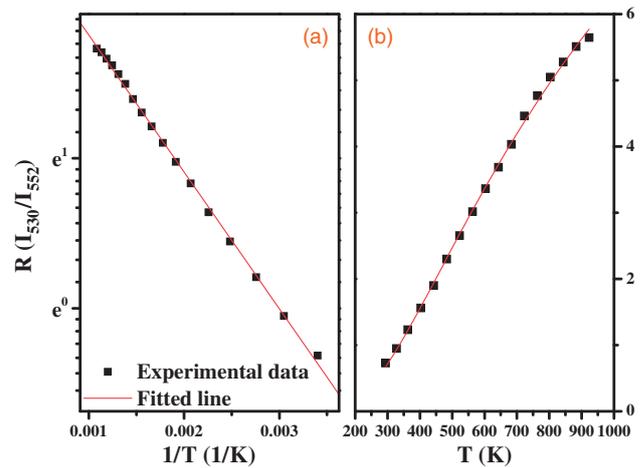


Fig. 3. (a) Monolog plot of FIR for Er<sup>3+</sup> green upconversion emissions vs the inverse of temperature; (b) behavior of FIR as a function of temperature.

a straight line with the corresponding  $\Delta E = 629.2 \pm 10$  cm<sup>-1</sup>. The FIR of the green UC emissions relative to the temperature is shown in Fig. 3(b). The value of the coefficient *C* in eq. (1) is  $15.43 \pm 0.06$  according to the fitting curve of the experimental data. Several temperature cycles had been tested and good repeatability was obtained.

For temperature sensing, it is important to know the rate at which the intensity ratio *R* changes for a change in temperature. This rate is known as the sensitivity *S* and defined as<sup>4)</sup>

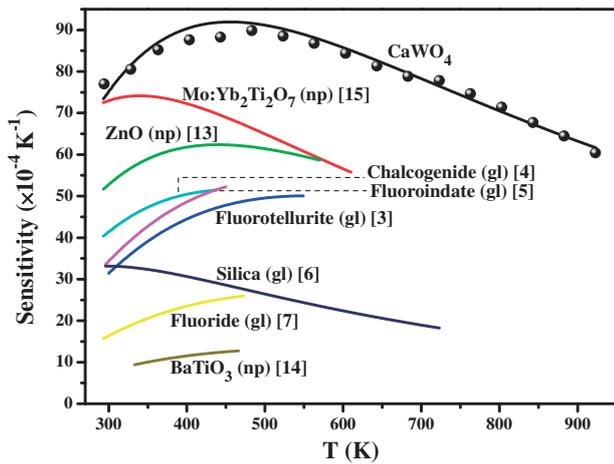
$$S = \frac{dR}{dT} = R \left( \frac{\Delta E}{k_B T^2} \right). \quad (2)$$

According to eq. (2), the sensitivity of the Er<sup>3+</sup>/Yb<sup>3+</sup>-codoped CaWO<sub>4</sub> phosphor is calculated and shown in Fig. 4. For comparison, the sensitivities of the other reported Er<sup>3+</sup>/Yb<sup>3+</sup>-codoped materials together with the measured temperature range are also presented. It is observed that the sensitivity of the Er<sup>3+</sup>/Yb<sup>3+</sup>-codoped CaWO<sub>4</sub> phosphor is much higher than those of the reported Er<sup>3+</sup>-fluorescence-based temperature sensors, and the maximum sensitivity of our sample is approximately 0.0092 K<sup>-1</sup> at 455 K. From eqs. (1) and (2), the sensitivity is determined by the factor *C* and  $\Delta E$ . The parameters *g*,  $\sigma$ , *w*, and  $\Delta E$  are known to be hardly influenced by changing the hosts. However, the ratio *A<sub>H</sub>*/*A<sub>S</sub>* will significantly vary in different host materials due to the hypersensitive transition: <sup>2</sup>H<sub>11/2</sub> → <sup>4</sup>I<sub>15/2</sub> to the surroundings,<sup>16)</sup> i.e., the parameter *C* changes from one host to another, and a larger value of *C* generally results in a higher sensitivity. Through comparison, the parameter *C* obtained in this work (*C* = 15.4) is larger than those of the literatures (*C* is in the range of 2.8–11.2),<sup>3–7,13–15)</sup> which is the main cause for the high sensitivity achieved here.

In addition, the measurement error is a significant factor for judging a temperature sensor, and it can be estimated from the calculated sensor sensitivity<sup>2,8)</sup>

$$\Delta T = \frac{\Delta R k_B T^2}{R \Delta E}. \quad (3)$$

A practical optical temperature sensing device requires a simple and inexpensive electronic circuit to process the ratio



**Fig. 4.** Calculated sensitivities (line) and measured values (circles) for the  $\text{Er}^{3+}/\text{Yb}^{3+}$ -codoped  $\text{CaWO}_4$  phosphor at temperatures from 294 to 923 K; the sensitivities of different  $\text{Er}^{3+}/\text{Yb}^{3+}$ -codoped materials together with the corresponding temperature measurement range are also presented (np: nanophosphors, gl: glass).

between the two light signals. Therefore, when employing a signal division circuitry with the same precision, a much smaller error can be expected by using the  $\text{Er}^{3+}/\text{Yb}^{3+}$ -codoped  $\text{CaWO}_4$  phosphor as the medium than by using previously reported materials.

Furthermore, another outstanding characteristic observed in our sample is the efficient green UC emissions. Even under a low pump power density ( $4.13 \text{ W}/\text{cm}^2$ ) of the 980 nm diode laser, the sample exhibited a very intense green luminescence at 294 K, as shown in the inset of Fig. 2. At 923 K, due to the thermal quenching effect, the green UC emission intensity is weakened, however, only goes down to about 2/7 of that at 294 K, and a bright green luminescence can still be clearly observed by the naked eyes, as shown in the corresponding photograph. It is worth to note that the doping content for  $\text{Er}^{3+}$  and  $\text{Yb}^{3+}$  ions is not optimized. The effect could be even better if the doping level is optimized.

In contrast, the green UC emissions of  $\text{Er}^{3+}$  in previously reported host materials<sup>6,13–15</sup> were greatly quenched at higher temperatures even if the pump power density of the 980 nm laser was about three orders of magnitude higher than that used in this work. With the good chemical and thermal stability of the  $\text{CaWO}_4$  phosphor, the upper limit

for temperature measurement is easily enhanced to 923 K without any degradation on the sample, and the other hosts cannot be used at such high temperatures (see Fig. 4). The efficient UC fluorescence of the  $\text{Er}^{3+}/\text{Yb}^{3+}$ -codoped  $\text{CaWO}_4$  phosphor is mainly attributed to two factors observed in the FT-IR spectra of our sample. First, the phonon threshold energy for  $\text{CaWO}_4$  is relatively low, about  $807 \text{ cm}^{-1}$ . Second, the introduction of  $\text{OH}^-$  group, which greatly quenches the luminescence of RE ions, is effectively decreased by the high-temperature solid-state reaction method. The efficient green UC emissions from the  $\text{Er}^{3+}/\text{Yb}^{3+}$ -codoped  $\text{CaWO}_4$  phosphor can provide a large signal-to-noise ratio and further improve the measurement accuracy.

In conclusion, by using the FIR technique, optical thermometry based on the green UC emissions of the  $\text{Er}^{3+}/\text{Yb}^{3+}$ -codoped  $\text{CaWO}_4$  phosphor was demonstrated in the temperature range of 294–923 K. The result suggests that the  $\text{Er}^{3+}/\text{Yb}^{3+}$ -codoped  $\text{CaWO}_4$  phosphor is a very good candidate for optical high-temperature sensors with higher sensitivity and better accuracy.

- 1) S. A. Wade, S. F. Collins, and G. W. Baxter: *J. Appl. Phys.* **94** (2003) 4743.
- 2) V. K. Rai: *Appl. Phys. B* **88** (2007) 297.
- 3) S. F. León-Luis, U. R. Rodríguez-Mendoza, E. Lalla, and V. Lavín: *Sens. Actuators B* **158** (2011) 208.
- 4) P. V. dos Santos, M. T. de Araujo, A. S. Gouveia-Neto, J. A. Medeiros Neto, and A. S. B. Sombra: *Appl. Phys. Lett.* **73** (1998) 578.
- 5) G. S. Maciel, L. de S. Menezes, A. S. L. Gomes, C. B. De Araujo, Y. Messaddeq, A. Florez, and A. Aegerter: *IEEE Photonics Technol. Lett.* **7** (1995) 1474.
- 6) C. R. Li, B. Dong, S. F. Li, and C. L. Song: *Chem. Phys. Lett.* **443** (2007) 426.
- 7) H. Berthou and C. K. Jørgensen: *Opt. Lett.* **15** (1990) 1100.
- 8) E. Maurice, G. Monnom, B. Dussardier, A. Saïssy, D. B. Ostrowsky, and G. W. Baxter: *Appl. Opt.* **34** (1995) 8019.
- 9) M. J. Treadaway and R. C. Powell: *J. Chem. Phys.* **61** (1974) 4003.
- 10) W. S. Cho, M. Yashima, M. Kakihana, A. Kudo, T. Sakata, and M. Yoshimura: *Appl. Phys. Lett.* **66** (1995) 1027.
- 11) Z. Piskuła, K. Staninski, and S. Lis: *J. Rare Earths* **29** (2011) 1166.
- 12) M. P. Hehlen, N. J. Cockroft, and T. R. Gosnell: *Phys. Rev. B* **56** (1997) 9302.
- 13) X. Wang, X. G. Kong, Y. Yu, Y. J. Sun, and H. Zhang: *J. Phys. Chem. C* **111** (2007) 15119.
- 14) M. A. R. C. Alencar, G. S. Maciel, C. B. de Araújo, and A. Patra: *Appl. Phys. Lett.* **84** (2004) 4753.
- 15) B. S. Cao, Y. Y. He, Z. Q. Feng, Y. S. Li, and B. Dong: *Sens. Actuators B* **159** (2011) 8.
- 16) C. K. Jørgensen and B. R. Judd: *Mol. Phys.* **8** (1964) 281.