Optical temperature sensing through the upconversion luminescence from Ho$^{3+}$/Yb$^{3+}$ codoped CaWO$_4$

Wei Xu$^a$, Hua Zhao$^b$, Yaxin Li$^c$, Longjiang Zheng$^c$, Zhiguo Zhang$^{a,d,*}$, Wenwu Cao$^{a,c,*}$

$^a$ Condensed Matter Science and Technology Institute, Harbin Institute of Technology, Harbin 150001, China
$^b$ School of Materials and Engineering, Harbin Institute of Technology, Harbin 150001, China
$^c$ Institute of Electrical Engineering, Yanshan University, Qinhuangdao 066004, China
$^d$ Laboratory of Sonos- and Photo-Theranostic Technologies, Harbin Institute of Technology, Harbin 150001, China
$^*$ Materials Research Institute, The Pennsylvania State University, PA 16802, USA

**ABSTRACT**

Under 980 nm diode laser excitation, efficient upconversion emissions from the Ho$^{3+}$/Yb$^{3+}$ codoped CaWO$_4$ phosphor were obtained. The upconversion quantum efficiency was evaluated to be about 3.3% when the power density of the excitation laser was 47 W/cm$^2$. Additionally, temperature dependent blue emissions from the $^5$F$_{2,3}$/$^5$K$_{6}$ and $^5$G$_{6}$/$^5$F$_{1}$ states of Ho$^{3+}$ ions were studied in the range of 303–923 K. The result demonstrated that using the ratio between the blue luminescence intensities of Ho$^{3+}$ ions, the sensitivity and the accuracy for optical thermometry achieved here are superior to the previously reported Er$^{3+}$ green fluorescence based optical temperature sensors.

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1. Introduction

Non-contact thermometry is a promising technique for temperature measurement [1,2]. This technique has been greatly stimulated by the requirement of safe, cheap, and reliable temperature sensing in the harsh environments, such as the electrical transformer in power stations, oil refineries, and coal mines, where the conventional contacting temperature measuring devices cannot be used. Actually, the non-contact temperature sensing devices can be realized via monitoring the fluorescence of materials with rare earth (RE) ions as the activators [3–5]. And the sensors based on the fluorescence intensity ratio (FIR) technique have recently attracted considerable attention for high sensitivity and accuracy measurement [3]. While developing a RE fluorescence based temperature sensor, upconversion (UC) emission would be more popular because it can be realized by excitation with a compact and cost-effective continuous wave near infrared diode laser. In addition, using the UC pumping method can effectively avoid the stray light, which is easily introduced by downconversion excitation source.

Ho$^{3+}$ is an excellent activator for infrared to short-wavelength (from ultraviolet to red) UC emissions because of its favorable intra-atomic 4f energy level structure and the relatively long-lived $^5$I$_1$ level that can act as a population reservoir for UC processes [6]. The energy gap between the $^5$F$_{2,3}$/$^5$K$_{6}$ and $^5$G$_{6}$/$^5$F$_{1}$ states of Ho$^{3+}$ is about 1300 cm$^{-1}$, indicating they are thermally coupled [3]. More importantly, blue emissions from these excited states can be obtained under the excitation of available 980 nm diode lasers [7,8]. Therefore, through the FIR between its blue emissions, Ho$^{3+}$ has potential to be used in optical thermometry. However, up to now, few reports about combinations of Ho$^{3+}$ ion with various hosts can be consulted in the field of temperature sensing. This is mainly because the thermal quenching effect on the UC emissions from the high energy states of Ho$^{3+}$ would become more serious with the increase of temperature, finally resulting in the difficulty in detecting the fluorescence signal at high temperatures. Therefore, choosing an appropriate host material seems to be a key factor to develop the temperature sensor based on the Ho$^{3+}$ luminescence. CaWO$_4$ has been thought to be one potential luminescent host due to its outstanding properties, including good chemical and physical stability, high density and reflection coefficient, as well as low phonon threshold energy [9–11]. Therefore, it is expected that CaWO$_4$ would be an ideal host for optical temperature sensing. In this work, the CaWO$_4$ phosphor with Ho$^{3+}$ as the activators was prepared, and Yb$^{3+}$ ions were added as the sensitizer due to the efficient energy transfer from Yb$^{3+}$ to Ho$^{3+}$. Intense UC emissions from the
sample were obtained under 980 nm diode laser excitation. The UC luminescence efficiency of the sample was studied using an integrating sphere. And the thermometry properties based on the blue UC emissions of Ho$^{3+}$ ions were investigated.

2. Experimental

The sample was prepared via high temperature solid-state reaction. CaO and WO$_3$ were mixed at 1:1 molar ratio, and 0.25 mol% Ho$_2$O$_3$–2.5 mol% Yb$_2$O$_3$ were added. The fully mixed chemicals are placed in a corundum crucible and then put into a SiC rods furnace to be heated to 800 ℃ and kept at this temperature for 3 h. Then, the materials are sintered in the furnace for 5 h at 1350 ℃ in an ambient atmosphere. The resulted phosphor was finally pressed into a thin disk. The crystal phase was confirmed by X-ray diffraction (XRD) method via a powder diffractometer (DMAX2500 Rigaku) using Cu Kα radiation ($\lambda = 0.15418$ nm). The UC luminescence spectra were recorded by Zolix-SBP300 grating spectrometer equipped with a CR131 photomultiplier tube. A 980 nm diode laser with a power- and temperature-controlled system (Thorlabs, JTC510 and TCLDM9) is used as the pump source. The quantum efficiency measurement of the samples is performed based on an integrating sphere (a barium sulfate coated integrating sphere 150 mm in diameter from Labsphere). To investigate the temperature dependent UC luminescence, the sample was placed in a mini homemade furnace and its temperature was increased from 303 to 923 K (the highest temperature of the furnace). The temperature of the sample was monitored by a copper-constantan thermocouple and controlled by a proportional-integral-derivative loop feedback temperature control system.

3. Results and discussion

Fig. 1 shows the XRD patterns for the CaWO$_4$ phosphor with and without Ho$^{3+}$/Yb$^{3+}$ ions. It can be seen that all the diffraction peaks for the RE doped CaWO$_4$ are in good agreement with those of the pure CaWO$_4$ phosphors, and both patterns can be well indexed to the standard PDF card No. 85-0443. No impurities or second phases were observed, indicating that single CaWO$_4$ phase was obtained. Fig. 2 shows the room temperature UC emission spectra of the Ho$^{3+}$/Yb$^{3+}$ codoped CaWO$_4$ phosphor under a 980 nm diode laser excitation with the pumping power of 150 mW. The sample exhibits intense green, red, and relatively weak near infrared emission bands of Ho$^{3+}$ ions, which are originated from the $^5$D$_{2}/^7$F$_{4}$ → $^7$I$_{6}$ ($\sim 550$ nm), $^5$D$_{2}$ → $^7$I$_{6}$ ($\sim 660$ nm), and $^5$D$_{2}/^7$F$_{4}$ → $^7$F$_{5}$ ($\sim 755$ nm) transitions, respectively. Furthermore, UC emissions centered at 363, 387, 423, 460, and 487 nm are successfully obtained in the samples. Such emissions can be attributed to the transitions from $^5$G$_{7/2}$/$^7$H$_{4}$, $^5$G$_{4}$/$^7$K$_{7}$, $^5$G$_{5}$/$^7$F$_{1}$, and $^5$F$_{2,3}$/^7$K$_{8}$ states of Ho$^{3+}$ to the $^7$K$_{8}$ ground state, respectively [7,8]. To better comprehend the mechanism population the emitting states and the radiative transitions corresponding to the UC emissions, the UC emission mechanism and population processes in Ho$^{3+}$/Yb$^{3+}$ codoped system are schematically illustrated in Fig. 3. Ho$^{3+}$ can give UC emissions without codoping Yb$^{3+}$ ions when excited by 980 nm laser, but the emission intensity is much weaker than that of Ho$^{3+}$/Yb$^{3+}$ codoped system [12]. Thus, successive energy transfer (ET) processes from Yb$^{3+}$ to Ho$^{3+}$ play an important role in promoting the Ho$^{3+}$ ions on the ground state to the excited states. Due to the small energy gaps from the $^5$G$_{5}$/$^7$H$_{6}$ and $^5$G$_{4}$/$^7$K$_{7}$ to their lower lying states, the $^5$G$_{5}$, $^5$G$_{6}$/$^7$F$_{1}$, and $^5$F$_{2,3}$/^7$K$_{8}$ levels are populated by the multiphonon nonradiative relaxations from the upper levels. Additionally, some cross-relaxation (CR) processes may also be involved [13,14].

During the experiment, it is observed that the Ho$^{3+}$/Yb$^{3+}$ codoped CaWO$_4$ exhibit bright UC emissions even the pumping power of the 980 nm laser is several milliwatt. Such phenomenon indicates that the sample possesses high luminescence efficiency. To understand the UC luminescence efficiency of the sample, the UC quantum efficiency is studied through a measurement setup based on the integrating sphere. The detailed measuring process is similar to that described in the work by our research group [15]. When the power density of 980 nm laser is 47 W/cm$^2$, the UC quantum efficiency of the sample is evaluated to be about 3.3%, which is comparable to that obtained in Er$^{3+}$/Yb$^{3+}$ codoped NaYF$_4$ (4%) [16]. The high luminescence efficiency could be mainly attributed to the low phonon threshold energy and the high reflection coefficient of CaWO$_4$ [9–11], which respectively contribute to the low nonradiative decay rates and high radiative emission rates of the RE energy levels.

Since intense blue emissions from the $^5$G$_{6}$/$^7$F$_{1}$ and $^5$F$_{2,3}$/^7$K$_{8}$ states of Ho$^{3+}$ are successfully obtained, the thermometry behavior based on the sample is studied. The temperature dependences of the blue emissions were measured in the range of 303–923 K. The pumping power of 980 nm diode laser was set at 150 mW. To guarantee the signal to noise ratio, the working voltage of the photomultiplier has been moderately increased. Fig. 4(a) shows the blue UC emission spectra at 303 and 923 K. It can be seen that the position of the emission bands hardly varies with the increase of temperature, but the intensity ratio between 460 and 487 nm emissions obviously changes. With the increase of temperature, the 460 nm emission intensity is greatly enhanced and about 4.4-fold enhancement is achieved at 773 K compared with that at room temperature. Although the 487 nm emission is weakened as temperature increases, high signal to noise ratio can be still obtained at 923 K. The change in the intensity ratio is attributed to the appropriate energy gap between the $^5$G$_{6}$/$^7$F$_{1}$ and $^5$F$_{2,3}$/^7$K$_{8}$ states, which allows the ions on $^5$F$_{2,3}$/^7$K$_{8}$ to be thermally populated onto $^5$G$_{6}$/$^7$F$_{1}$ states with the increase of temperature. According to the literature [3], the FIR from the thermally coupled levels (TCL) of RE ions is modified as

$$\text{FIR} = \frac{I_i}{I_j} = A \exp \left( -\frac{\Delta E}{k_B T} \right) + B,$$

where $I_i$ and $I_j$ are intensities for emissions from the upper and the lower TCL; $A$ and $B$ are constant; $\Delta E$ is the energy difference between TCL; $k_B$ is the Boltzmann constant, and $T$ is the absolute temperature. The temperature dependence of the FIR between the 460 and 487 nm is plotted in Fig. 4(b). The experimental data are fitted using Eq. (1). It can be seen that the fittings agree well with the experimental data. The parameters $A$ and $B$ are fitted to be about $16.67 \pm 1.2$ and $0.23 \pm 0.01$, respectively, and $\Delta E$ is fitted to be about $1304 \pm 50$ cm$^{-1}$, closing to the value obtained from the emission.
Fig. 2. Upconversion luminescence spectra of the Ho\textsuperscript{3+}/Yb\textsuperscript{3+} codoped CaWO\textsubscript{4} phosphor under excitation of 980 nm diode laser with the power of 150 mW.

Several temperature circles have been tested and a good reproducibility was obtained.

For optical thermometry, it is of great importance to understand the rate at which the FIR changes for a change in temperature $T$. This parameter is known as the sensitivity. To allow the comparison between the sensitivities obtained from the FIR of different TCL, the absolute sensitivity $S_a$ is defined as $[3,17]$

$$S_a = \frac{\Delta E}{k_B T^2}. \tag{2}$$

Eq. (2) suggests that using pairs of levels with larger energy difference results in a higher sensitivity. Previously, most attention has been paid to the temperature sensors based on the green emissions from the thermally coupled $^2\text{H}_{11/2}$ and $^4\text{S}_{3/2}$ states of Er\textsuperscript{3+} in various materials $[18-25]$. For comparison, the sensitivities for those sensing materials and that achieved in this work are presented in Table 1. It can be seen that the sensitivity obtained in this work is higher than those of the Er\textsuperscript{3+} green fluorescence based sensors in the same temperature range. This is mainly resulted from the larger energy gap between the thermally coupled $^5\text{G}_0/\text{F}_1$ and $^5\text{F}_{2,3}/\text{K}_8$ states of Ho\textsuperscript{3+} ions, which is also in favor of high measurement resolution.

Considering practical applications, it is also necessary to know the variation of sensitivity with temperature. For this purpose, the relative sensitivity $S_r$ has been defined as $[19,20]$

$$S_r = \text{FIR} \times \frac{\Delta E}{k_B T^2}. \tag{3}$$

Fig. 3. The energy level diagram of the Ho\textsuperscript{3+} and Yb\textsuperscript{3+} ions as well as the proposed upconversion mechanisms.
Fig. 4. (a) Blue upconversion emission spectra of Ho\(^{3+}\) at 303 and 923 K, respectively; (b) fluorescence intensity ratio between the blue emissions of Ho\(^{3+}\) ions plotted as a function of temperature. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Table 1

<table>
<thead>
<tr>
<th>Activator: sensing materials</th>
<th>Transitions</th>
<th>(S_r (K^{-1}))</th>
<th>Temperature range (K)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ho(^{3+}): CaWO(_4)</td>
<td>(^4)I(<em>{15}/2) K(</em>{6}), (^4)G(<em>{5}/2) F(</em>{1}) (\rightarrow) (^4)I(_{8})</td>
<td>1890/T(^2)</td>
<td>303–923</td>
<td>This work</td>
</tr>
<tr>
<td>Er(^{3+}): fluorotellurite glass</td>
<td>(^2)H(<em>{11}/2), (^4)S(</em>{3}/2) (\rightarrow) (^4)I(_{15}/2)</td>
<td>1036/T(^2)</td>
<td>300–550</td>
<td>[18]</td>
</tr>
<tr>
<td>Er(^{3+}): BaTiO(_3)</td>
<td>(^2)H(<em>{11}/2), (^4)S(</em>{3}/2) (\rightarrow) (^4)I(_{15}/2)</td>
<td>940/T(^2)</td>
<td>322–466</td>
<td>[19]</td>
</tr>
<tr>
<td>Er(^{3+}): chalcogenide glass</td>
<td>(^2)H(<em>{11}/2), (^4)S(</em>{3}/2) (\rightarrow) (^4)I(_{15}/2)</td>
<td>928/T(^2)</td>
<td>293–498</td>
<td>[20]</td>
</tr>
<tr>
<td>Er(^{3+}): ZnO</td>
<td>(^2)H(<em>{11}/2), (^4)S(</em>{3}/2) (\rightarrow) (^4)I(_{15}/2)</td>
<td>880/T(^2)</td>
<td>273–573</td>
<td>[21]</td>
</tr>
<tr>
<td>Er(^{3+}): Y(_2)SiO(_5)</td>
<td>(^2)H(<em>{11}/2), (^4)S(</em>{3}/2) (\rightarrow) (^4)I(_{15}/2)</td>
<td>817/T(^2)</td>
<td>300–600</td>
<td>[22]</td>
</tr>
<tr>
<td>Er(^{3+}): Cd(_2)O(_3)</td>
<td>(^2)H(<em>{11}/2), (^4)S(</em>{3}/2) (\rightarrow) (^4)I(_{15}/2)</td>
<td>746/T(^2)</td>
<td>300–900</td>
<td>[23]</td>
</tr>
<tr>
<td>Er(^{3+}): Y(_2)Ti(_2)O(_7)</td>
<td>(^2)H(<em>{11}/2), (^4)S(</em>{3}/2) (\rightarrow) (^4)I(_{15}/2)</td>
<td>679/T(^2)</td>
<td>296–610</td>
<td>[24]</td>
</tr>
<tr>
<td>Er(^{3+}): silicate glass</td>
<td>(^2)H(<em>{11}/2), (^4)S(</em>{3}/2) (\rightarrow) (^4)I(_{15}/2)</td>
<td>592/T(^2)</td>
<td>296–723</td>
<td>[25]</td>
</tr>
</tbody>
</table>

judging a temperature sensor, can be estimated from the relative sensitivity \(S_r\) using the following equation [26]

\[
\Delta T = \Delta \text{FIR} \times k_B T^2
\]

In a practical optical temperature sensing device, a simple and inexpensive electronic circuit is usually required to process the ratio between the two light signals. And from Eq. (4), it is known when employing a signal division circuitry with the same precision, larger \(S_r\) results in smaller error. Through comparing with the Er\(^{3+}\) green luminescence based sensors [18–25], it can be known that due to the larger \(S_r\) at higher temperature, better accuracy can be still expected in high temperature range using the blue emissions from the Ho\(^{3+}\)/Yb\(^{3+}\) codoped CaWO\(_4\) phosphor. Combined with the good chemical and physical stability as well as high luminescence efficiency, the Ho\(^{3+}\)/Yb\(^{3+}\) codoped CaWO\(_4\) is a promising candidate for optical thermometry.

4. Conclusions

Efficient UC emissions from Ho\(^{3+}\) ions in Ho\(^{3+}\)/Yb\(^{3+}\) codoped CaWO\(_4\) phosphor were obtained when excited by 980 nm laser. The quantum efficiency of the sample has been preliminarily studied and was estimated to be about 3.3% using an integrated sphere. In addition, the blue UC emissions from the Ho\(^{3+}\): \(^5\)G\(_{5}/2\)F\(_1\) and \(^5\)F\(_{2,3}\)K\(_{6}\) states were studied as a function of temperature ranging from 303 to 923 K. The result illustrates that an excellent optical
temperature sensor with high sensitivity, high resolution, and good accuracy can be designed based on the Ho³⁺/Yb³⁺ codoped CaWO₄.

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References


Biographies

Wei Xu is currently pursuing his PhD under the supervision of Prof. Zhang and Prof. Cao. His research is focused on the development of luminescent materials doped with rare earth ions and their luminescence properties at high temperatures for the application on the optical thermometry.

Hua Zhao is an associate professor of material science. Her current interest includes preparation methods on biomedical materials and upconverting luminescent materials.

Yaxin Li is pursuing his MD under the supervision of Prof. Zheng. Her research is focused on the measuring and testing technologies and instruments.

Longjiang Zheng is a professor of electronics. His current research includes the technology and application for laser spectroscopy as well as photoelectric detection technology.

Zhiguang Zhang is a professor of physics. He has authored more than 100 articles on topics of the detection of radioactive lifetime in rare earth ions. His current research interest includes upconverting luminescent materials, fluorescent biosensing and the detection of harmful gas density.

Wenwu Cao is a professor of Mathematics and Materials Science. He has authored more than 350 articles on topics of functional material. His current research interest includes the design on optical sensors, ultrasonic transducers, novel piezoelectric materials and medical therapeutic ultrasound.