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An optical temperature sensor based on the upconversion luminescence from Tm^{3+}/Yb^{3+} codoped oxyfluoride glass ceramic

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ABSTRACT

An optical temperature sensor based on the upconversion luminescence of Tm^{3+} has been developed. Under a 980 nm diode laser excitation, the fluorescence intensity ratio (FIR) between 700 (Tm^{3+}:$^3F_{2,3} \rightarrow {}^3H_6$) and 800 nm ($Tm^{3+}$:$^3H_4 \rightarrow {}^3H_6$) upconversion emissions from Tm^{3+}/Yb^{3+} codoped oxyfluoride glass ceramic was studied as a function of temperature in the range of 293–703 K. The $^3F_{2,3}$ and $^3H_4$ states of Tm^{3+} are verified to be thermally coupled levels. By using FIR technique, the sensitivity for detecting temperature variations achieved here is better than previous reported rare earth ions fluorescence based temperature sensors. With the advantages of intense upconversion luminescence and absolutely separated 700 and 800 nm emission bands, the Tm^{3+}/Yb^{3+} codoped oxyfluoride glass ceramic is a very promising candidate for accurate optical temperature sensors with much higher sensitivity and resolution.

1. Introduction

Optical temperature sensors based on the fluorescence of rare earth (RE) ions have attracted great interest in recent years [1]. This technique provides a non-contact temperature measurement by probing the temperature dependence of fluorescence intensities. Compared with conventional temperature monitoring devices, fluorescence based thermometry system does not affect the temperature field and is particularly advantageous operating in electromagnetically and/or thermally harsh environments, such as at electrical power stations, near high power electric transmission lines, and remote temperature detection in buildings on fire.

As an optical thermometry method, the fluorescence intensity ratio (FIR) technique is based on the measurement of fluorescence intensities from two thermally coupled levels (TCL) of one kind RE ions, which is independent of spectrum losses and fluctuations in the excitation intensity, consequently leading to a much higher accuracy. It is known that the fluorescence of RE ions can be generated through upconversion (UC) or downconversion mechanism via proper pumping. When developing a RE fluorescence based temperature sensor, UC emission is more popular because it can be realized by excitation with a compact and cost-effective continuous wave near infrared diode laser. Furthermore, the stray light, which is easily introduced by downconversion excitation source to affect the temperature measurement, can be effectively avoided by using the UC pumping method. Some RE ions, including Er^{3+}, Pr^{3+}, Nd^{3+}, and Yb^{3+}, have already been used as the activators for optical temperature sensors based on the UC luminescence from their corresponding TCL [1–5].

We found that intense 700 (Tm^{3+}:$^3F_{2,3} \rightarrow {}^3H_6$) and 800 nm ($Tm^{3+}$:$^3H_4 \rightarrow {}^3H_6$) UC emissions can be obtained in Tm^{3+}/Yb^{3+} codoped oxyfluoride glass ceramic [6]. From its absorption spectra, the energy difference ΔE between $^3F_{2,3}$ and $^3H_4$ is evaluated to be about 1850 cm^{-1}, which matches the situation of TCL, 200 $cm^{-1} \leq \Delta E_{TCL} \leq 2000\ cm^{-1}$ [1]. However, no attention has been paid to Tm^{3+} ions in the application of optical thermometry, mainly because the weak 700 nm light signal is very difficult to detect. In this work, we have successfully enhanced the intensity of the 700 nm UC luminescence of Tm^{3+} and studied the temperature dependence of emissions centered at 700 and 800 nm from Tm^{3+}/Yb^{3+} codoped oxyfluoride glass ceramic under the excitation of a 980 nm diode laser. Our results indicated that by using the FIR technique, Tm^{3+}/Yb^{3+} codoped oxyfluoride glass ceramic has great potential to be used as optical temperature sensor with various advantages over the existing RE fluorescence based sensors.

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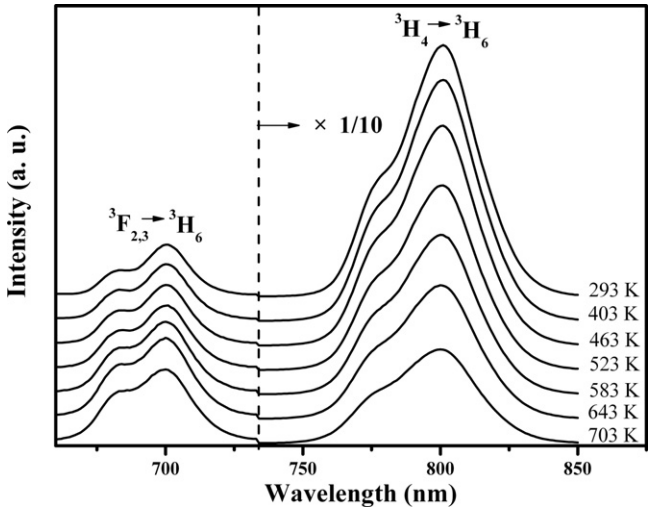

Fig. 1. UC emission spectra of Tm^{3+}/Yb^{3+} codoped oxyfluoride glass ceramic in the wavelength range of 650–850 nm at various temperatures.

2. Experimental

The precursor glass with molar compositions of $50SiO_2$–$50PbF_2$–$0.25Tm_2O_3$–$2.5Yb_2O_3$ was prepared by using high-purity SiO_2, PbF_2, Tm_2O_3 and Yb_2O_3 powders. The detailed synthesis process is similar to our previous work [6]. The resulting sample is cut and polished into the size of 10 mm × 8 mm × 1.5 mm. The UC luminescence spectra were recorded by Zolix-SBP300 grating spectrometer equipped with CR131 photomultiplier. A 980 nm diode laser, whose working temperature is set at 293 K by a temperature controller, is used as the pump source. To investigate the temperature dependent UC luminescence, the sample was placed in a silica tube, which is then put into a mini furnace composed with SiC rods. The temperature of sample was monitored by a copper-constantan thermocouple with measurement error of ±1.5 K and controlled by a proportional–integral–derivative loop feed back temperature control system. To avoid the change in the crystallization of the oxyfluoride glass ceramic, the heating upper limit is set below the crystallization temperature (753 K).

3. Results and discussion

Fig. 1 shows the UC luminescence spectra in the wavelength range of 650–850 nm for Tm^{3+}/Yb^{3+} co-doped oxyfluoride glass ceramic at different temperatures. The pump power of 980 nm laser diode is set as 150 mW. It can be seen that the spectra exhibit two distinct luminescence bands centered at 700 and 800 nm, which are attributed to the $^3F_{2,3} \rightarrow {}^3H_6$ and $^3H_4 \rightarrow {}^3H_6$ transitions of Tm^{3+} ions [6]. Fig. 2 shows the energy level diagrams of Tm^{3+} and Yb^{3+}, as well as the UC mechanism for generating 700 and 800 nm UC luminescence. Since the pumping photon of 980 nm laser can only be absorbed by Yb^{3+} ions, two successive energy transfer processes are needed to populate the $^3F_{2,3}$ states. The $^3H_4$ state is then populated by the nonradiative relaxation from the $^3F_{2,3}$ states, resulting in the intense 800 nm near infrared emission. From Fig. 1, it also can be observed that the peak positions of these two emission bands are hardly changed with temperature, but the emission intensities for 700 and 800 nm emissions respond differently to the change of temperature. The 800 nm emission intensity gradually decreases with the increase of temperature, while the intensity for 700 nm red emission increases greatly and about twofold enhancement is achieved at 643 K. To verify that the $^3F_{2,3}$ and $^3H_4$ are TCL, the FIR between 700 and 800 nm emission at various temperatures was calculated.

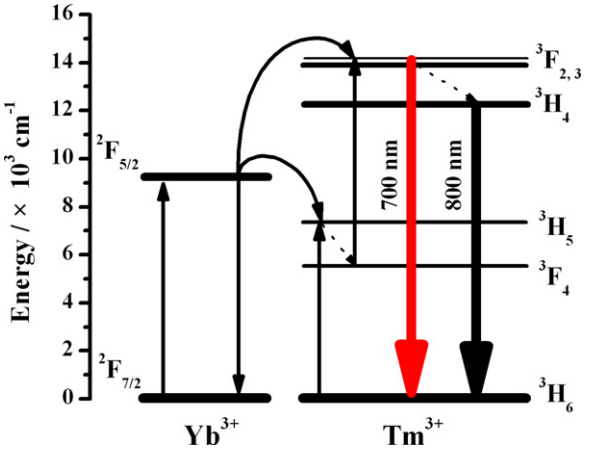

Fig. 2. Energy level diagram for Tm^{3+} and Yb^{3+} as well as the upconversion mechanisms for Tm^{3+}/Yb^{3+} codoped system.

According to the theory by Wade et al. [1], the FIR for the emissions from TCL of RE ions can be written as:

$$\mathrm{FIR} = \frac{I_i}{I_j} = A \exp\left(-\frac{\Delta E}{k_B T}\right) + B \quad (1)$$

where I_i and I_j are intensities for emissions from the upper and the lower TCL; A and B are constants; ΔE is the energy difference between these two levels; k_B is the Boltzmann constant, and T is the absolute temperature. Fig. 3 shows the plot of the FIR between 700 and 800 nm UC luminescence vs. temperature in the range of 293–703 K. The experimental data are fitted by using Eq. (1). It can be seen that the fitting matches well with the experimental data. The fitted coefficients A and B in Eq. (1) are about 2.78 and 0.014, respectively, and ΔE is fitted to be about 1952 cm^{-1}, very close to the experimental value 1850 cm^{-1}. These results confirm that the $^3F_{2,3}$ and $^3H_4$ of Tm^{3+} are TCL. In addition, we have also studied the behavior of the FIR at different excitation powers, and the ratio remains unchanged for powers up to 200 mW.

For thermometry applications, it is of great importance to know the sensitivity, which is reflected by the rate of change in the FIR in response to the variation of temperature. The sensitivity S is defined as [1,7]:

$$S = \frac{1}{R}\frac{dR}{dT} = \frac{\Delta E}{k_B T^2} \quad (2)$$

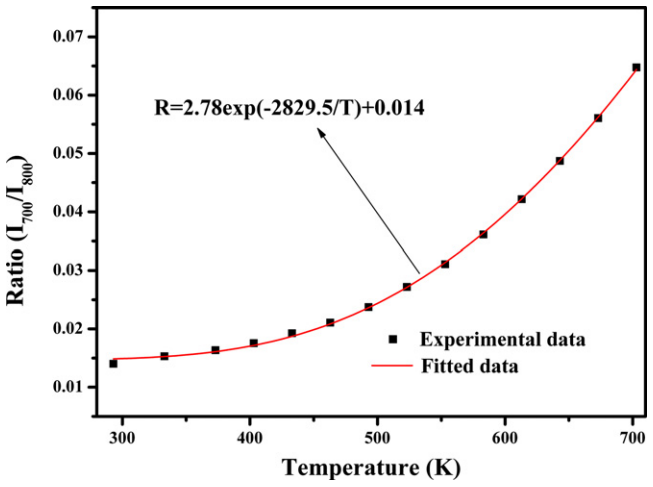

Fig. 3. FIR of upconversion emissions at 700 and 800 nm vs. temperature in the range of 293–703 K.

Table 1
Values of the sensitivity for different RE ions in different host materials are presented, and the involved transitions from TCL as well as temperature range are included.

Rare earth (host)	Transitions	Sensitivity (K^{-1})	Temperature range (K)	Reference
Tm^{3+} (oxyfluoride glass ceramic)	$^3F_{2,3}$, $^3H_4 \rightarrow {}^3H_6$	$2829.5/T^2$	293–703	This work
Er^{3+} (chalcogenide glass)	$^2H_{11/2}$, $^4S_{3/2} \rightarrow {}^4I_{15/2}$	$928.9/T^2$	293–498	Ref. [4]
Pr^{3+} (tellurite glass)	$^3P_1 + {}^1I_6$, $^3P_0 \rightarrow {}^3H_5$	$879.9/T^2$	293–473	Ref. [9]
Nd^{3+}(borosilicate glass)	$^4F_{3/2}$, $^4F_{5/2} \rightarrow {}^4I_{9/2}$	$1691.3/T^2$	296–670	Ref. [3]
Sm^{3+}(silica)	$^4F_{3/2}$, $^4G_{5/2} \rightarrow {}^6H_{5/2}$	$1593.2/T^2$	295–748	Ref. [1]
Dy^{3+}(silica)	$^4I_{15/2}$, $^4F_{9/2} \rightarrow {}^6H_{13/2}$	$1546.7/T^2$	295–523	Ref. [1]
Eu^{3+}(silica)	$^5D_1$, $^5D_0 \rightarrow {}^7F_1$	$2648.2/T^2$	101–673	Ref. [1]

From Eq. (2), in the certain temperature range, the sensitivity S is in proportion to the energy difference between the TCL. Table 1 presents the expressions of sensitivity for our sample and the materials doped with other RE activators. It can be seen that the sensitivity value for Tm^{3+}/Yb^{3+} codoped oxyfluoride glass ceramic is much higher than other RE ions fluorescence based sensors at the same temperature. This high sensitivity is attributed to the much larger energy gap between the $^3F_{2,3}$ and $^3H_4$ states of Tm^{3+} ions, which is also beneficial for obtaining higher measurement resolution. Therefore, it can be concluded that by employing the same experimental equipments, sensors based on Tm^{3+}/Yb^{3+} codoped oxyfluoride glass ceramic are expected to exhibit much higher sensitivity and resolution for temperature measurements than those applying other RE ions doped materials.

Meanwhile, it is worth to note that owing to the much larger energy separation between the $^3F_{2,3}$ and $^3H_4$ states of Tm^{3+}, the thermalizing rate from the $^3H_4$ to the $^3F_{2,3}$ states will be reduced at lower temperatures. And in contrast, other radiative or nonradiative process may dominate the thermalization process, consequently leading to the "decoupling" effect on the two states, i.e. the $^3F_{2,3}$ and the $^3H_4$ states cannot be deemed as fully thermally coupled at low temperatures, which is similar to the case of $^5D_0$ and $^5D_1$ states of Eu^{3+} [1]. This phenomenon has been observed in our experiment, where the FIR between 700 and 800 nm emissions at 293 K exhibits a relatively large deviation from the prediction of Eq. (1). The deviation would be more apparent for the FIR at low temperatures. Therefore, it is more appropriate to use Tm^{3+} as the activator for high temperature measurement.

Furthermore, some other superior properties observed in our sample should be noted:

(1). When considering practical applications, it is also necessary to understand the change of sensitivity with temperature. Through Eq. (1), the theoretical sensitivity S_T is gained as:

$$S_T = \frac{dR}{dT} = R\left(\frac{\Delta E}{k_B T^2}\right) \quad (3)$$

The corresponding value for our sample is shown in Fig. 4. It can be seen that the sensitivity keeps increasing in our experimental temperature range. Similar enhancement behavior of sensitivity with temperature was also observed in the previous reports [2–4,8], but those reported sensitivities at higher temperatures are much worse.

(2). Because of the low phonon energy environment in the fluoride nanocrystals and the large separation of $^3H_4$ state from the lower lying $^3H_5$ state (about 4723 cm^{-1}), the 700 and 800 nm UC emissions from Tm^{3+}/Yb^{3+} codoped oxyfluoride glass ceramic are difficult to be thermally quenched. Bright 700 nm red luminescence can be observed by naked eyes even when the temperature is as high as 703 K. Such efficient luminescence is of great benefit for achieving adequate signal to noise ratio at high temperatures.

(3). It can be seen from Fig. 1 that the emission bands centered at 700 and 800 nm are absolutely separated in the oxyfluoride glass ceramic. While the emission bands from TCL of the other RE ions (Er^{3+}, Pr^{3+}, Sm^{3+}, Eu^{3+}, Yb^{3+}, Dy^{3+}) are all overlapping to some extent [1]. Band overlapping would cause the measured FIR to deviate from the behavior predicted by Eq. (1), resulting in larger detection error. The absolutely separated UC emission bands from $^3F_{2,3}$ to $^3H_4$ state of Tm^{3+} are in favor of a thermometry with much improved accuracy.

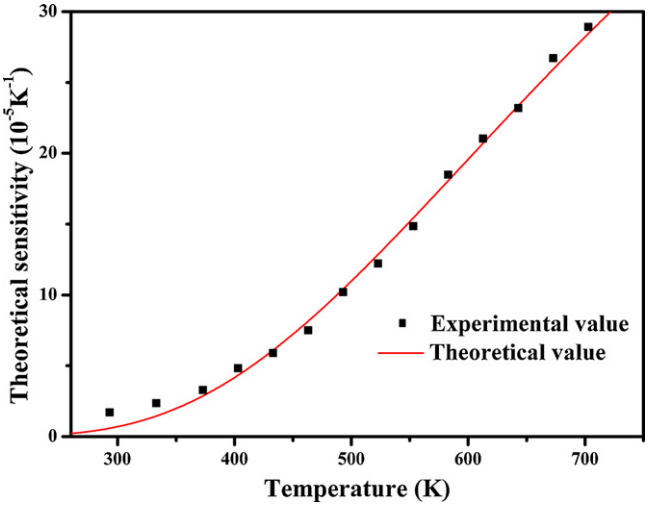

Fig. 4. Theoretical sensitivity as a function of temperature in the temperature range of 293–703 K.

4. Conclusions

Under a 980 nm diode laser excitation, 700 and 800 nm UC emissions from Tm^{3+} in Tm^{3+}/Yb^{3+} co-doped oxyfluoride glass ceramic were studied at temperatures ranging from 293 to 703 K. By using FIR method, $^3F_{2,3}$ and $^3H_4$ state of Tm^{3+} were verified as TCL. The application of Tm^{3+} for optical temperature sensor was discussed utilizing the much enhanced 700 nm emission intensity. It was found that the sensitivity for thermometry achieved here is much higher than previous reported optical temperature sensors based on the same technology. With other superior properties, such as the efficient UC emissions and the absolutely separated 700 and 800 nm emission bands, the Tm^{3+}/Yb^{3+} co-doped oxyfluoride glass ceramic is an excellent candidate for developing novel optical temperature sensors, which can give much high sensitivity, better resolution and good accuracy.

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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.

Xiaoyang Gao is pursuing his MD under the supervision of Prof. Zheng. His research is focused on the measuring and testing technologies and instruments.

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Zhiguo Zhang is a professor of physics. He has authored more than 100 articles on topics of the detection of radiative 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 physics. He has authored more than 200 articles on topics of ferroelectric material. His current research interest includes the design on optical transducer, novel piezoelectricity materials and medical ultrasonic transducer.