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

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A B S T R A C T

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.

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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 $\Delta E$ 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.
2. Experimental

The precursor glass with molar compositions of 50SiO$_2$–50PbF$_2$–0.25Tm$_2$O$_3$–2.5Yb$_2$O$_3$ was prepared by using high-purity SiO$_2$, PbF$_2$, Tm$_2$O$_3$, and Yb$_2$O$_3$ 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 $^3$F$_{2,3} \rightarrow ^3$H$_6$ and $^3$H$_4 \rightarrow ^3$H$_6$ transitions of Tm$^{3+}$ ions [6]. 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 $^3$F$_{2,3}$ states. The $^3$H$_4$ state is then populated by the nonradiative relaxation from the $^3$F$_{2,3}$ states, resulting in the intense 800 nm near infrared emission. From Fig. 1, it can also 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 $^3$F$_{2,3}$ and $^3$H$_4$ are TCL, the FIR between 700 and 800 nm emission at various temperatures was calculated.

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

$$\text{FIR} = \frac{l_i}{l_j} = A \exp \left( -\frac{\Delta E}{k_B T} \right) + B \quad (1)$$

where $l_i$ and $l_j$ are intensities for emissions from the upper and the lower TCL; $A$ and $B$ are constants; $\Delta E$ is the energy difference between these two levels; $k_B$ is the Boltzmann constant, and $T$ is the absolute temperature. Fig. 2 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 $\Delta E$ is fitted to be about 1952 cm$^{-1}$, very close to the experimental value 1850 cm$^{-1}$. These results confirm that the $^3$F$_{2,3}$ and $^3$H$_4$ 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. 1. UC emission spectra of Tm$^{3+}$/Yb$^{3+}$ codoped oxyfluoride glass ceramic in the wavelength range of 650–850 nm at various temperatures.](image1)

![Fig. 2. Energy level diagram for Tm$^{3+}$ and Yb$^{3+}$ as well as the upconversion mechanisms for Tm$^{3+}$/Yb$^{3+}$ codoped system.](image2)

![Fig. 3. FIR of upconversion emissions at 700 and 800 nm vs. temperature in the range of 293–703 K.](image3)
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 Tm3+/Yb3+ co-doped oxfluoride 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 3F2,3 and 3H4 states of Tm3+, which is also beneficial for obtaining higher measurement resolution. Therefore, it can be concluded that by employing the same experimental equipments, sensors based on Tm3+/Yb3+ co-doped oxfluoride 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 3F2,3 and 3H4 states of Tm3+, the thermalizing rate from the 3H4 to the 3F2,3 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 3F2,3 and the 3H4 states cannot be deemed as fully thermally coupled at low temperatures, which is similar to the case of 5D0 and 5D1 states of Eu3+ [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 Tm3+ 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:

\[
S_T = \frac{dR}{dT} = R \left( \frac{\Delta E}{k_B T^2} \right)
\]

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 3H4 state from the lower lying 3H5 state (about 4723 cm\(^{-1}\)), the 700 and 800 nm UC emissions from Tm3+/Yb3+ co-doped oxfluoride 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 oxfluoride glass ceramic. While the emission bands from TCL of the other

| RE ions (Er3+, Pr3+, Sm3+, Eu3+, Yb3+, Dy3+) 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 3F2,3 to 3H4 state of Tm3+ are in favor of a thermometer with much improved accuracy.

4. Conclusions

Under a 980 nm diode laser excitation, 700 and 800 nm UC emissions from Tm3+ in Tm3+/Yb3+ co-doped oxfluoride glass ceramic were studied at temperatures ranging from 293 to 703 K. By using FIR method, 3F2,3 and 3H4 state of Tm3+ were verified as TCL. The application of Tm3+ 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 Tm3+/Yb3+ co-doped oxfluoride 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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References

Biographies

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