Highly sensitive optical thermometry through thermally enhanced near infrared emissions from Nd$^{3+}$/Yb$^{3+}$ codoped oxyfluoride glass ceramic

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ABSTRACT

Under 980 nm diode laser excitation, the near infrared (NIR) emissions originated from the $^4F_{7/2}$/$^4I_{9/2}$ → $^4I_{9/2}$ (750 nm), $^4F_{5/2}$/$^4I_{9/2}$ → $^4I_{9/2}$ (803 nm), and $^4F_{5/2}$ → $^4I_{9/2}$ (863 nm) transitions of Nd$^{3+}$ ions in Nd$^{3+}$/Yb$^{3+}$ codoped oxyfluoride glass ceramic were obtained and studied as a function of temperature in the range of 303–623 K. It was observed that these NIR emissions were greatly enhanced with the increase of temperature. An explanation based on the luminescence decay curves was given, and it was found that the thermally enhanced phonon-assisted energy transfer (ET) from Yb$^{3+}$ to Nd$^{3+}$ played an important role in such phenomenon. In addition, by using the fluorescence intensity ratio technique, the optical thermometry behavior based on the NIR emissions of Nd$^{3+}$ ions was investigated. Using the 750 and 863 nm emissions from the Nd$^{3+}$/Yb$^{3+}$ codoped glass ceramic, higher sensitivity for temperature measurement can be achieved compared to the previous reported rare earth ions fluorescence based optical temperature sensors. Due to its thermally enhanced NIR emissions, the Nd$^{3+}$/Yb$^{3+}$ codoped oxyfluoride glass ceramic is a promising candidate for optical temperature sensors with high sensitivity and good accuracy.

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1. Introduction

In recent years, optical temperature sensing devices based on the fluorescence of material with rare earth (RE) ions as the activators have attracted much interest [1,2]. Research in this field has been stimulated by increasing demand for safe, cheap, and reliable sensors in the monitoring of electrical transformer temperature in power stations, oil refineries, coal mines, and building fire detections, where contacting types temperature measurement techniques cannot be used. 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 and consequently leads to much higher measurement accuracy and reliability.

Owing to the presence of suitable TCL ($^4F_{5/2}$/$^4H_{9/2}$ and $^4F_{3/2}$), Nd$^{3+}$ is promising in applications in optical thermometry by using its NIR emissions [2,3]. Nd$^{3+}$ has large absorption cross-section at 800 nm, so the lasers centered around this wavelength were usually used to excite the Nd$^{3+}$ doped sensing medium. However, the overlapping of the pumping laser band and the emission band of Nd$^{3+}$ ions results in a relatively large temperature detection error [2]. Although the Nd$^{3+}$ ions can be excited by short-wavelength lasers to avoid the overlapping effect, the expensive pumping source and the stray light caused by short-wavelength lasers limit the practical applications of Nd$^{3+}$ ions on optical temperature sensors. Therefore, it is necessary to develop a doping system, in which the NIR emissions of Nd$^{3+}$ ions can be generated by excitation with a compact and cost-effective continuous wave NIR diode lasers without overlapping with the NIR emissions.

Due to the large absorption cross-section around 980 nm, Yb$^{3+}$ ions are usually utilized as the sensitizer to help gain the efficient emissions from other RE ions, such as Er$^{3+}$, Ho$^{3+}$, and Tm$^{3+}$, when excited by a 980 nm laser. However, the study on the ET from Yb$^{3+}$ to Nd$^{3+}$ to enhance the NIR emissions from Nd$^{3+}$ ions when excited by 980 nm laser is limited. In this work, the Nd$^{3+}$/Yb$^{3+}$ codoped system was designed and synthesized, and the oxyfluoride glass ceramic was selected as the host material due to its low phonon energy and good chemical and physical stability [4,5]. The result shows that the NIR emissions of Nd$^{3+}$ ions centered at 750, 803 and 863 nm can be readily obtained in this glass ceramic when excited by a 980 nm diode laser. Interestingly, these emissions can be greatly enhanced
with the increase of temperature. An explanation based on the temperature dependent luminescence decay curves was given. In addition, optical thermometry based on the NIR fluorescence was evaluated. Our results indicated that the Nd$^{3+}$/Yb$^{3+}$ codoped oxyfluoride glass ceramic has a great potential to be used as an optical temperature sensor with various advantages over other existing RE fluorescence based sensors.

2. Experimental

The raw materials of the precursor glass were composed of high-purity SiO$_2$ and PbF$_2$ at 1:1 molar ratio, and 0.1 mol% Nd$_2$O$_3$ and 1.5 mol% Yb$_2$O$_3$ were added. The detailed preparing process is similar to our previous work [6]. The resulting samples were cut and polished for optical measurements. X-ray diffraction (XRD) patterns were acquired using a Rigaku D/max-γB diffractometer with Cu Kα radiation (λ = 0.15418 nm). The luminescence spectra were recorded using Zolix-SBP300 grating spectrometer equipped with CR131 photomultiplier. The absorption spectra were recorded by using a spectrophotometer (Perkin-Elmer, Lambda 900). 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 dependence of luminescence, the sample was placed in a silica tube, which is then put into a home-made mini furnace made of 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 feedback temperature control system. The luminescence decay curves were measured by the 980 nm diode laser modulated through square-wave electric current and recorded by Tektronix DPO 4140 oscilloscope. When measuring the luminescence decay curves of the infrared emissions from Yb$^{3+}$ ions, the light signal was detected by InGaAs photodiode. 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

The XRD patterns of the precursor glass and the glass ceramic are shown in Fig. 1. It can be seen that there are only two humps in the XRD curve for the glass, indicating its amorphous structure. However, after thermal treatment, intense diffraction peaks attributed to β-PbF$_2$ nanocrystals emerge in the XRD patterns [7], reflecting the crystallization during thermal treatment. Fig. 2 shows the NIR fluorescence spectra of the Nd$^{3+}$/Yb$^{3+}$ codoped glass and glass ceramic under 980 nm laser excitation with a power of 260 mW. Two emission bands centered at 803 and 863 nm, originated from the $^4F_{5/2}^2H_{9/2}$ → $^4I_{9/2}$ and $^4F_{3/2}^2 → ^4I_{9/2}$ transitions of Nd$^{3+}$ ions, respectively, were obtained in the precursor glass. In the glass ceramic, these two emissions are enhanced, and a fluorescence band centered at 750 nm, which was not observed in the previous works [2,3], is also obtained. From the absorption spectra of the Nd$^{3+}$/Yb$^{3+}$ codoped glass ceramic in the inset of Fig. 2, the 750 nm emission is originated from the $^4F_{7/2}^2S_{5/2} → ^4I_{9/2}$ transitions of Nd$^{3+}$ ions. Compared with the absorption spectra, the wavelengths corresponding to the emission spectra peaks exhibit red shift. This phenomenon is known as Stokes shift, which is due to the energy loss of the Nd$^{3+}$ ions on the levels resulting from the lattice vibrations. Here, it is worth to note that no NIR emissions were detected in samples singly doped with Nd$^{3+}$ ions, indicating that the ET from Yb$^{3+}$ to Nd$^{3+}$ plays an important role in generating the luminescence of Nd$^{3+}$ ions. The enhancement of the NIR emissions in the oxyfluoride glass ceramic is generally attributed to two contributions. First, some RE ions will be incorporated into the fluoride nanocrystals during the thermal treatment [8], and the lower phonon energy environment of the fluoride nanocrystals can weaken the multi-phonon nonradiation relaxation and is in favor of increasing luminescence intensity. Second, the distance between the RE ions will be shortened in the fluoride nanocrystals. According to the Dexter theory [9], the ET from Yb$^{3+}$ to Nd$^{3+}$ will be strengthened and subsequently contributes to the enhancement of the NIR fluorescence from Nd$^{3+}$ ions.

The energy level diagrams of the Yb$^{3+}$ and Nd$^{3+}$ ions as well as the possible emission mechanisms for the Nd$^{3+}$/Yb$^{3+}$ codoped system are shown in Fig. 3. Since the 980 nm pumping photons can only be efficiently absorbed by Yb$^{3+}$ ions, ET processes are needed

![Image](image_url)
to populate the emission states of Nd$^{3+}$ ions. Due to the energy mismatch between the $4F_{3/2}$ level of Yb$^{3+}$ and the $4F_{3/2}$ level of Nd$^{3+}$, the ET from Yb$^{3+}$ to Nd$^{3+}$ is a phonon-assisted process [10]. From the absorption spectra in the inset of Fig. 2, it can be seen that the energy gaps between the $4F_{3/2}$ and $4F_{5/2}^22H_{9/2}$ ($\Delta E\approx 960$ cm$^{-1}$), the $4F_{3/2}$ and $4F_{7/2}/4S_{3/2}$ ($\Delta E\approx 1910$ cm$^{-1}$), and the $4F_{5/2}^22H_{9/2}$ and $4F_{7/2}/4S_{3/2}$ states ($\Delta E\approx 1020$ cm$^{-1}$) are relatively small, so that the $4F_{3/2}^22H_{9/2}$ and $4F_{7/2}/4S_{3/2}$ states can be populated by thermal population from their lower energy levels. Also, the NIR emitting levels can be populated by nonradiative relaxations from the upper states because of the small energy differences [11].

To understand the properties related to optical temperature sensors, the temperature dependent NIR emissions from Nd$^{3+}$ in Nd$^{3+}$/Yb$^{3+}$ codoped glass ceramic was studied in the temperature range of 303–623 K, and the pumping power of 980 nm diode laser was set at 260 mW. The emission spectra at different temperatures are shown in Fig. 4. It is interesting to observe that the intensities for these emissions are greatly enhanced as temperature rises without changing the peak positions of the emissions. One important fact is that the rates of intensity increase with temperature for different peaks in the NIR emission spectrum are different. Compared to the intensities at 303 K, enhancement in the intensity up to 187, 50, and 8-fold can be achieved at 623 K for the 750, 803, and 863 nm emissions, respectively. As discussed above, the ET from Yb$^{3+}$ to Nd$^{3+}$ ions is phonon-assisted, hence this kind ET process will be strengthened with the increase of temperature [12]. Because of this, the population in the $4F_{3/2}$ state of Nd$^{3+}$ will be increased as temperature rises and finally leads to thermal enhancement for the 863 nm emission. Due to the small energy differences from the $4F_{3/2}$ to $4F_{5/2}^22H_{9/2}$ and the $4F_{7/2}/4S_{3/2}$ states, more ions will be thermally populated in the $4F_{7/2}/4S_{3/2}$ and $4F_{5/2}^22H_{9/2}$ states with the increase of temperature, resulting in the enhancement of the 750 and 803 nm NIR emission intensities.

The thermally enhanced ET rates from Yb$^{3+}$ to Nd$^{3+}$ may be understood by using the following equation [10]:

$$W_{Yb\rightarrow Nd} = \frac{1}{\tau_{Yb\rightarrow Nd}} - \frac{1}{\tau_{Yb}},$$

where $W_{Yb\rightarrow Nd}$ is the ET rate from Yb$^{3+}$ to Nd$^{3+}$; $\tau_{Yb\rightarrow Nd}$ and $\tau_{Yb}$ are the lifetimes of the $2F_{5/2}$ state of Yb$^{3+}$ in the Nd$^{3+}$/Yb$^{3+}$ singly doped and Yb$^{3+}$ singly doped glass ceramic, respectively. The corresponding luminescence decay curves for $2F_{5/2}$ state of Yb$^{3+}$ at different temperatures are presented in Fig. 5(a). Based on the curves, the temperature dependent ET rates from Yb$^{3+}$ to Nd$^{3+}$ ions are estimated by Eq. (1) and the results are illustrated in Fig. 5(b). It can be clearly observed that the ET rate from Yb$^{3+}$ to Nd$^{3+}$ is greatly enhanced with the increase of temperature. Although the multiphonon nonradiative relaxations of Nd$^{3+}$ ions will be increased with temperature and the back ET from Nd$^{3+}$ to Yb$^{3+}$ may also take place, it can be concluded from Fig. 4 that these effects are not dominant in the experiment temperature range.

As discussed above, the relative change in the intensities with temperature change for the NIR emissions is different. This phenomenon is attributed to the thermally coupled relations between the $4F_{7/2}/4S_{3/2}$, $4F_{5/2}^22H_{9/2}$, and $4F_{3/2}$ levels of Nd$^{3+}$ ions. In other words, due to the small energy gaps, the thermally coupled $4F_{7/2}/4S_{3/2}$ and $4F_{3/2}$ levels (TCL1), $4F_{7/2}/4S_{3/2}$ and $4F_{5/2}^22H_{9/2}$ levels (TCL2), as well as $4F_{5/2}^22H_{9/2}$ and $4F_{3/2}$ levels (TCL3) can all be used for the application of optical thermometry by using FIR technique. Below, the FIR emission from the corresponding TCL of Nd$^{3+}$ ions in Nd$^{3+}$/Yb$^{3+}$ codoped glass ceramic at various temperatures are calculated.

According to the literatures [1,13], the FIR for the emissions from TCL of RE ions can be written as

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

(2)

where $l_i$ and $l_j$ are intensities of emissions from the upper and the lower TCL; A and B are constants; $\Delta E$ is the energy difference between TCL; $k_B$ is the Boltzmann constant, and $T$ is the absolute temperature. Fig. 6 shows the plot of the FIR between the 750 and 863 nm, 750 and 803 nm as well as 803 and 863 nm luminescence vs. temperature in the range of 303–623 K. The FIR is obtained through the ratio between the integrated areas under the corresponding emission spectra. The experimental data are fitted to Eq. (2) and the fitting parameters are presented in Fig. 6. It can be seen that the fitting curve matches well with the experimental data. The values of $\Delta E$ between TCL1, TCL2 and TCL3 are fitted to be about 2076, 1300, and 1216 cm$^{-1}$, respectively, close to the corresponding experimental value (1910, 1020, and 960 cm$^{-1}$) deduced from the absorption spectra. 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 with temperature. This value is known as the sensitivity. To allow the comparison between

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**Fig. 5.** (a) Luminescence decay curves of the Yb$^{3+}$ ($2F_{5/2}$) at 303 and 623 K obtained from the Yb$^{3+}$ doped and Nd$^{3+}$/Yb$^{3+}$ codoped glass ceramic. (b) Energy transfer rate from Yb$^{3+}$ to Nd$^{3+}$ at different temperatures.
Fig. 6. Fluorescence intensity ratios between the NIR emissions at temperatures ranging from 303 to 623 K.

Fig. 7. The sensitivities based on the different thermally coupled levels of Nd³⁺ ions in Nd³⁺/Yb³⁺ codoped glass ceramic.

Sensitivities obtained from the FIR of different TCL, the absolute sensitivity $S$ is defined as follows [1,14].

$$ S = \frac{\Delta E}{kT^2} $$

Eq. (3) suggests that using pairs of levels with larger energy difference is in favor of higher sensitivity. The sensitivities for Nd³⁺/Yb³⁺ codoped glass ceramic by the different TCL of Nd³⁺ ions are expressed in Table 1 and shown in Fig. 7. For comparison, the expressions of the sensitivities for other RE ions doped materials are also presented Table 1. It can be seen that by utilizing the thermally coupled $4F_{7/2}/4S_{3/2}$ and $4F_{3/2}$ levels of Nd³⁺ ions, the sensitivity achieved here is much higher than other RE ions fluorescence based sensors. This high sensitivity is attributed to the much larger energy gap between the $4F_{7/2}/4S_{3/2}$ and $4F_{3/2}$ levels, which is also beneficial for obtaining higher measurement resolution. Here, it should be noted that, similar to the case of Eu³⁺ and Tm³⁺ [1,15], the “decoupling” effect will become more obvious for the $4F_{7/2}/4S_{3/2}$ and $4F_{3/2}$ levels of Nd³⁺ ions at lower temperatures owing to the much larger energy separation. This effect would make the FIR between 750 and 863 nm emissions deviate from the prediction of Eq. (2) and result in a relatively large measurement error. Therefore, it is more appropriate to use the 750 and 863 nm emissions for high-temperature measurement. At lower temperature range, the measurement can be performed by using the emissions from the thermally coupled $4F_{7/2}/4S_{3/2}$ and $4F_{5/2}/2H_{9/2}$ levels or the thermally coupled $4F_{5/2}/2H_{9/2}$ and $4F_{3/2}$ levels, which possess smaller energy gaps.

Considering practical applications, it is also necessary to understand the change of sensitivity with temperature. Through Eq. (2), the relative sensitivity $S_R$ is defined as

$$ S_R = \frac{d\text{FIR}}{dT} = \text{FIR} \left( \frac{\Delta E}{kT^2} \right). $$

The corresponding values for our sample are shown in Fig. 8. It can be seen that when using TCL1, the sensitivity keeps increasing in our experimental temperature range and will theoretically achieve the maximum at 1505 K. Similar enhancement of sensitivity with temperature was also observed in previous reports [1,17,18], but those reported sensitivities at higher temperatures are much worse.

Additionally, compared to previous reported optical temperature sensors based on the fluorescence of RE ions doped materials, another outstanding advantage achieved here is the

Table 1

<table>
<thead>
<tr>
<th>Rare earth (host)</th>
<th>Transitions</th>
<th>Sensitivity (K⁻¹)</th>
<th>Temperature range (K)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nd³⁺ (oxyfluoride glass ceramic)</td>
<td>$4F_{7/2}/4S_{3/2}$, $4F_{3/2}$ → $4I_{15/2}$</td>
<td>3010.1/T²</td>
<td>303–623</td>
<td>This work</td>
</tr>
<tr>
<td></td>
<td>$4F_{7/2}/2H_{11/2}$, $4F_{3/2}$ → $4I_{11/2}$</td>
<td>1763.2/T²</td>
<td>303–623</td>
<td>This work</td>
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<tr>
<td></td>
<td>$4F_{7/2}/5I_{15/2}$, $4F_{5/2}/2H_{9/2}$ → $4I_{15/2}$</td>
<td>1884.6/T²</td>
<td>303–623</td>
<td>This work</td>
</tr>
<tr>
<td>Tm³⁺ (oxyfluoride glass ceramic)</td>
<td>$3P_{2/1}/1H_{4}/1P_{1/2}$ → $1H_{6}$</td>
<td>2829.5/T²</td>
<td>293–703</td>
<td>Ref. [13]</td>
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<tr>
<td>Ho³⁺ (oxyfluoride glass ceramic)</td>
<td>$4I_{15/2}$, $4I_{11/2}$ → $3H_{9}$</td>
<td>2238.6/T²</td>
<td>303–643</td>
<td>Ref. [16]</td>
</tr>
<tr>
<td>Er³⁺ (chalcogenide glass)</td>
<td>$2H_{15/2}$, $4I_{15/2}$ → $4I_{13/2}$</td>
<td>928.9/T²</td>
<td>293–498</td>
<td>Ref. [17]</td>
</tr>
<tr>
<td>Pr³⁺ (tellurite glass)</td>
<td>$3P_{2/1}/1I_{6}$, $3P_{0}/1I_{4}$ → $1H_{6}$</td>
<td>879.7/T²</td>
<td>293–473</td>
<td>Ref. [18]</td>
</tr>
<tr>
<td>Sm³⁺ (silica)</td>
<td>$4F_{5/2}$, $4G_{9/2}$ → $4H_{15/2}$</td>
<td>1593.2/T²</td>
<td>295–748</td>
<td>Ref. [1]</td>
</tr>
<tr>
<td>Dy³⁺ (silica)</td>
<td>$4I_{15/2}$, $4I_{11/2}$ → $4I_{13/2}$</td>
<td>1546.7/T²</td>
<td>295–523</td>
<td>Ref. [1]</td>
</tr>
<tr>
<td>Eu³⁺ (silica)</td>
<td>$5D_{1/2}$, $5D_{3/2}$ → $7F_{1}$</td>
<td>2648.2/T²</td>
<td>101–673</td>
<td>Ref. [1]</td>
</tr>
</tbody>
</table>

This work

References [1,16,18]
thermal enhancement of NIR fluorescence. Based on reported works [1,15–18], it is known that thermal quenching effect on the emissions from the RE ions doped sensing mediums becomes stronger with the increase of temperature. This phenomenon will make it difficult to detect the fluorescence signal at high temperatures, resulting in low signal-to-noise ratio and high measurement error. On the other hand, the thermally enhanced NIR emissions from Nd\(^{3+}/\)Yb\(^{3+}\) codoped glass ceramic can provide strong light signal even at high temperatures so that the sample is promising for accurate thermometry applications.

4. Conclusions

An optical temperature sensor based on the Nd\(^{3+}/\)Yb\(^{3+}\) doped oxyfluoride glass ceramic has been developed. Under a 980 nm diode laser excitation, 750, 803, and 863 nm emissions from Nd\(^{3+}\) in Nd\(^{3+}/\)Yb\(^{3+}\) doped glass ceramic were obtained and investigated at temperatures ranging from 303 to 623 K. It was observed that the emissions are greatly enhanced with the increase of temperature, which is mainly attributed to thermally enhanced energy transfer from Yb\(^{3+}\) to Nd\(^{3+}\) ions. This is advantageous to compare other RE based temperature sensors since in general fluorescence intensities decrease with temperature. When utilizing the thermally coupled \(^{4}F_{7/2}^{\text{exc}}\)\(^{4}S_{3/2}\) and \(^{4}F_{3/2}\) levels of Nd\(^{3+}\) ions, the sensitivity for thermometry achieved here is much higher than other reported optical temperature sensors based on the FIR technique due to larger energy gap. With these superior properties, the Nd\(^{3+}/\)Yb\(^{3+}\) doped glass ceramic is an excellent candidate for making optical temperature sensors, which can give much higher sensitivity, higher resolution and better accuracy compared to the existing RE fluorescence based temperature sensors.

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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 for the application on the optical thermometry.

Hua Zhao is an associate professor of material science. She has authored more than 20 articles on inorganic materials. Her current research interest includes preparation methods on bio-medical materials and upconverting luminescent materials.

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