Optical temperature sensor based on up-conversion fluorescence emission in Yb^{3+}:Er^{3+} co-doped ceramics glass*

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Yb^{3+}:Er^{3+} co-doped oxy-fluoride ceramics glass has been prepared. The mechanism of up-conversion emissions about Er^{3+} was discussed, and the temperature properties of green up-conversion fluorescence between 303 and 823 K were investigated. The results show that the sensitivity of this sample reaches its maximum value, about 0.0047 K^{-1}, when the temperature is 383 K, indicating that this kind of sample can be used as high temperature and high sensitivity optical temperature sensor.

Keywords: Yb^{3+}:Er^{3+} co-doped ceramics glass, up-conversion emission, optical temperature sensor

PACC: 7840, 3280K

1. Introduction

Due to the lower cost, more compactable and longer life, optical temperature sensors are attracting more interest than conventional devices in the operation in thermally, chemically, and electromagnetically hazardous environments. Some have already been applied to temperature monitoring in highly corrosive media, electrical power stations, oil refiners, coal mines, and building fire detections.[1−4] Temperature detectors based on fluorescence intensity ratio (FIR) of rare earth (RE) ions have been extensively investigated in recent years. For suitable level structure and luminescence properties, many researches have focused on the trivalent erbium ions, and lots of investigations on optical temperature sensors of different materials doped with Er^{3+} have been reported recently.[5−7]

One of the most important aspects to be considered when developing the temperature sensing detectors is the RE doped host materials. On one hand, the host material should provide high up-conversion efficiency under moderate excitation power. On the other hand, it should possess the capability to withstand the high temperature environment also. Among many candidates, the oxy-fluoride ceramics glasses are one of the new kinds of host materials with the advantages of oxide glasses and fluoride glasses, such as higher transparency, better chemical stabilization and higher temperature resistance. Furthermore, many studies have revealed that the RE ions would embed in fluoride microcrystal after heat treatment, and the phonon energy can get lower.[8,9] In this work, we report the investigation on the Yb^{3+}:Er^{3+} co-doped oxy-fluoride ceramics glass, and study the thermal properties of up-conversion emissions between 303 and 823 K. The results indicate that this material shows great prospect in practical application in high temperature and high sensitivity optical temperature sensors.

2. Experiment

The Yb^{3+}:Er^{3+} co-doped oxy-fluoride ceramics glass was prepared by high temperature sintering technique as described in the literatures.[10,11] The original compositions of the ceramics glass substrate are 40-mol%SiO_2–20-mol%Al_2O_3–40-mol%PbF_2, and the dopant concentrations of the RE ions are respectively 1-mol%Er_2O_3 and 2.5-mol%Yb_2O_3. After grinding adequately, the mixed materials were put into a crucible which is placed in the furnace to be heated at

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1060 °C for 1 h. Then the liquid materials were poured onto a steel plate and put into another muffle furnace for heat treatment at nucleus formation temperature for 8 h. The glass sample was formed after that. The sensor temperature was raised from 303 to 823 K by placing the sample in an oven, which was heated by resistive wire elements. A copper-constantan thermocouple was attached to one face of the glass to monitor the sensor temperature. The up-conversion emissions of visible spectra were measured with a universal system composed of detectors with different wavebands, a monochromator, and a lock-in amplifier and so on. A 980-nm semiconductor laser diode was used as pump power.

3. Results and discussion

3.1. Up-conversion emissions analysis

A typical up-conversion spectrum of radiation originating from the Yb^{3+}:Er^{3+} co-doped ceramics glass in the wavelength region of interest, at 303 and 823 K is depicted in Fig. 1.

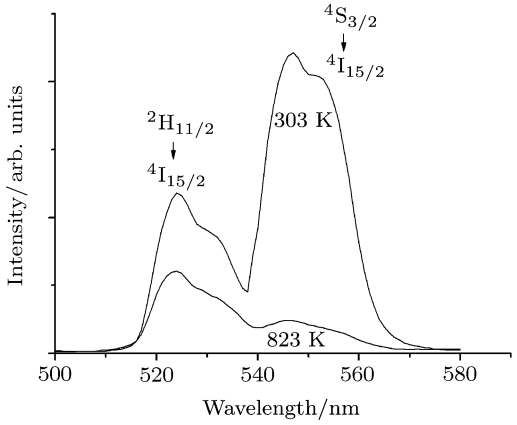


Fig. 1. Green up-conversion emissions spectra at different temperature excited by 980-nm laser.

The up-conversion spectra present the two distinct green emission signals around 523 nm and 547 nm, respectively corresponding to the $^2H_{11/2}$ and $^4S_{3/2}$ transitions to the ground state $^4I_{15/2}$ of erbium ions. In Fig. 1, it can be seen that the corresponding wavelengths of the green up-conversion do not change but the intensities get weaker as temperature increases. The relation between both green up-conversion emissions intensities and pump power follows the law: $I \propto I_{\text{pump}}^n$. From Fig. 2 we can see that the slopes are respectively 2.5 and 2.0 for the green up-conversion emissions centred at about 523 nm and 547 nm, clearly meaning that two-photon process is involved in green up-conversions.

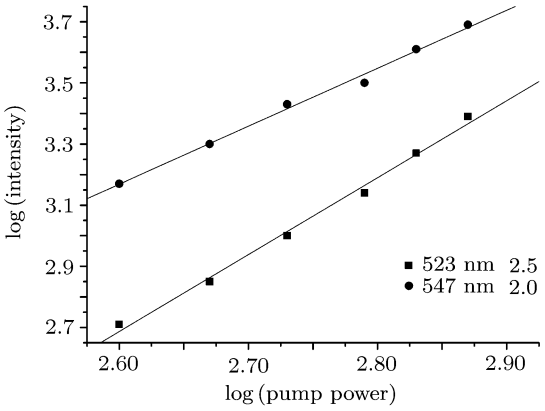


Fig. 2. The dependence of peak intensity of the green up-conversion emissions on the pump power in logarithmic scale.

Figure 3 shows the mechanism of green up-conversion emissions. The particle population in the excited energy level $^2H_{11/2}$ and $^4S_{3/2}$ of Er^{3+} is achieved by the two-photon process, containing energy transfer (ET), ground state absorption (GSA), excited state absorption (ESA) and cross relaxation (CR).[12−14] The green up-conversion emissions process can be described as:

$$\text{GSA}: {}^4I_{15/2}(Er^{3+}) + \text{a photon} \rightarrow {}^4I_{11/2}(Er^{3+});$$
$$\text{ET1}: {}^4I_{15/2}(Er^{3+}) + {}^2F_{5/2}(Yb^{3+}) \rightarrow {}^4I_{11/2}(Er^{3+}) + {}^2F_{7/2}(Yb^{3+});$$
$$\text{ESA}: {}^4I_{11/2}(Er^{3+}) + \text{a photon} \rightarrow {}^4F_{7/2}(Er^{3+});$$
$$\text{ET2}: {}^4I_{11/2}(Er^{3+}) + {}^2F_{5/2}(Yb^{3+}) \rightarrow {}^4F_{7/2}(Er^{3+}) + {}^2F_{7/2}(Yb^{3+});$$
$$\text{CR}: {}^4I_{11/2}(Er^{3+}) + {}^4I_{11/2}(Er^{3+}) \rightarrow {}^4I_{15/2}(Er^{3+}) + {}^4F_{7/2}(Er^{3+}).$$

The Er^{3+} ions on the energy level $^4F_{7/2}$ relax to $^2H_{11/2}$ and $^4S_{3/2}$ rapidly, and then transit to the ground state respectively, emitting the 523-nn and 547-nm green light.

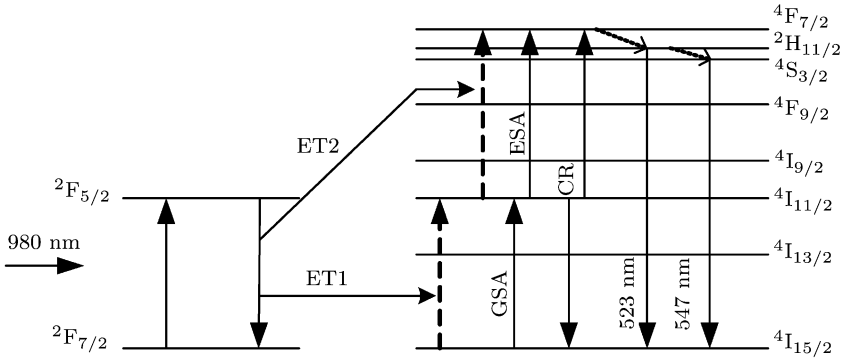


Fig. 3. Schematic diagram of green up-conversion emissions pumped by 980-nm laser.

3.2. Studies on the temperature properties

Based on the theory of Boltzmann, the particle population density on the energy level $^2H_{11/2}$ and $^4S_{3/2}$ can be written as

$$\frac{n_H}{n_S} = \frac{g_H}{g_S}\exp\left(-\frac{E_H - E_S}{kT}\right) = \frac{g_H}{g_S}\exp\left(-\frac{\Delta E}{kT}\right), \quad (1)$$

where the parameters n_H, n_S, g_H, g_S are the particle densities and degeneracy factors of the energy level $^2H_{11/2}$ and $^4S_{3/2}$ respectively. And $\Delta E = E(^2H_{11/2}) - E(^4S_{3/2})$ is the energy gap, k is the Boltzmann constant, T is the absolute temperature. Generally, $E(^2H_{11/2})$ is bigger than $E(^4S_{3/2})$, i.e., n_H is less than n_S. Therefore, the transition intensity of $^2H_{11/2} \rightarrow {}^4I_{15/2}$ is weaker than that of $^4S_{3/2} \rightarrow {}^4I_{15/2}$, as shown in spectra at 303 K in Fig. 1. But with increasing temperature, energy separation between $^2H_{11/2}$ and $^4S_{3/2}$ allows the $^2H_{11/2}$ level to be populated by thermal agitation, resulting in the transition intensity about $^2H_{11/2} \rightarrow {}^4I_{15/2}$, getting stronger than that of $^4S_{3/2} \rightarrow {}^4I_{15/2}$, as presented in the spectra of Fig. 1 at 823 K. However, due to the increase of temperature, the whole green up-conversion emission intensities become smaller.

The fluorescence intensity ratio (FIR) can be written as follows:[15]

$$\mathrm{FIR} \equiv R = \frac{I_H}{I_S} = \frac{g_H\sigma_H\omega_H}{g_S\sigma_S\omega_S}\exp\left(-\frac{\Delta E}{kT}\right), \quad (2)$$

where I_H and I_S are respectively the transition intensities of $^2H_{11/2} \rightarrow {}^4I_{15/2}$ and $^4S_{3/2} \rightarrow {}^4I_{15/2}$. The parameters σ_H, σ_S, ω_H, ω_S are emission cross sections, transition angular frequencies of energy levels $^2H_{11/2}$ and $^4S_{3/2}$; g_H, g_S, ΔE, k and T are defined as the same as those in Eq. (1).

The sensitivity of the optical temperature sensor is defined as[16]

$$S = \frac{\mathrm{d}R}{\mathrm{d}T} = R\left(-\frac{\Delta E}{kT^2}\right). \quad (3)$$

In order to prevent the glass getting softening and guarantee the accuracy of the experiment, the highest working temperature is set at 823 K. The relation curve between green fluorescence intensity ratio of Er^{3+} ions and T can be fitted through Eq. (2), and the fitting formula is $R = 6.62\exp(-785.07/T)$, as presented in Fig. 4.

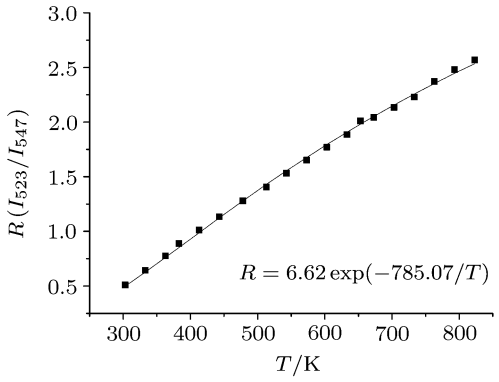


Fig. 4. Relation between R and working temperature.

The results illustrated in Fig. 4 clearly show that the intensity ratio increases as the sample's temperature rises. The sensitivity is calculated through Eq. (3), and the results are shown in Fig. 5. It can be known that when the temperature is 383 K, the sensitivity reaches its maximum, about 0.0047 K^{-1}, and its minimum is about 0.0030 K^{-1} at $T = 823$ K. It is worth while to point out that, at the same temperature, the values of sensitivity are all bigger than those of Yb^{3+}:Er^{3+} co-doped and Yb^{3+}:Er^{3+}:Nd^{3+}

co-doped Al_2O_3 powder reported recently by our study group,[17,18] and the highest working temperature in the present paper approaches that (913 K)

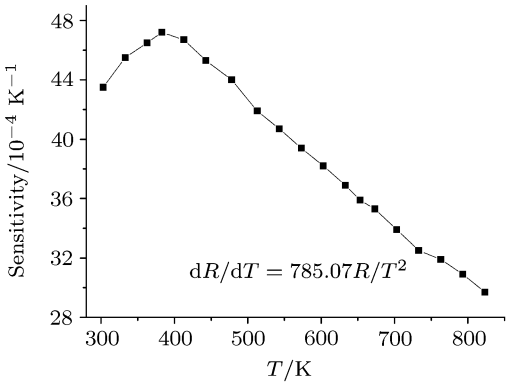


Fig. 5. Relation between sensitivity and working temperature.

reported in an Er^{3+}-doped SiO_2 optical device,[19] implying that our sample is suitable for preparing high temperature and high sensitivity optical temperature sensor.

4. Conclusions

Yb^{3+}:Er^{3+} co-doped oxy-fluoride ceramics glass has been prepared by high temperature melting technique. The mechanism of green up-conversion emissions and the temperature properties of Er^{3+} between 303 and 823 K are investigated. The relation between fluorescence intensity ratio R and temperature T is fitted as $R = 6.62\exp(-785.07/T)$, and the value of sensitivity becomes biggest, about 0.0047 K^{-1}, when the temperature is 383 K. Furthermore, the temperature properties are better than those we reported before, and the highest working temperature is comparatively greater, indicating that this kind of sample shows great prospect in making high temperature and high sensitivity optical temperature sensor.

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