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Researching on thermal characters in Yb^{3+}/Er^{3+} codoped phosphate glass ceramic for fluorescence temperature sensor

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ABSTRACT

To explore fluorescence temperature sensor, Yb^{3+}/Er^{3+} co-doped phosphate glass ceramic was prepared by high-temperature melting method and thermal annealing technology. The luminescent spectra of the sample were measured under 975 nm excitation at the temperature ranges of 25–300 °C. The strong green up-conversion emissions, coming from the transitions of Er^{3+} ion: $^2H_{11/2}$-$^4I_{15/2}$ and $^4S_{3/2}$-$^4I_{15/2}$, were observed. The fluorescence intensity ratio of the two green up-conversion emissions can change with the increasing of temperature. The sensitivity of Er^{3+}/Yb^{3+} co-doped phosphate glass ceramic reached the maximal value of ~0.0077 K^{-1}. The sensitivity is relatively flat at the high temperature region. Our research is valuable to developing fluorescence temperature sensor.

Introduction

The materials doped rare-earth ions have been widely researched because of their abundant energy level structures in the visible and infrared wavelength regions [1–6]. Their unique optical properties had shown the potential application values in color display, white light-emitting diode, fluorescent labeling, laser amplifier, in vivo imaging, and so on [7–10]. Trivalent Er^{3+} doped materials had revealed good up-conversion emission characters, and attracted people's attention [11–13]. Under ~980 nm excitation, the materials doped with Er^{3+} ion can emit two green up-conversion emissions, which come from the transition of Er^{3+} ion: $^4S_{3/2}$-$^4I_{15/2}$ and $^2H_{11/2}$-$^4I_{15/2}$. The energy level gap of two green emissions is very near (~500 cm^{-1}). Thus, the relative population of the two energy levels can be affected by the environmental temperature. The ground state absorption cross-section of Er^{3+} ion at ~980 nm is low (about 1.7×10^{-21} cm^2), which leads to reduction of up-conversion emissions. Considering the large absorption cross-section of Yb^{3+} ion at ~980 nm (about 11.7×10^{-21} cm^2), Yb^{3+} ion is usually co-doped into Er^{3+} doping materials as sensitizer. Since the optical temperature sensor based on the fluorescence intensity ratio, Er^{3+}/Yb^{3+} co-doped glasses and nanopowders have been reported [14–16]. However, the reports on Er^{3+}/Yb^{3+} co-doped glass ceramics applying to fluorescence temperature sensor are few. In this letter, the Er^{3+}/Yb^{3+} co-doped phosphate glass ceramic had been prepared. And the up-conversion emission spectra of the materials have been studied in detail.

Experimental

The phosphate glass ceramic with the composition of $60P_2O_5$–$20CaO$–$10Li_2O$–$9Al_2O_3$–$0.25Er_2O_3$–$0.75Yb_2O_3$ (wt%) was prepared by the high-temperature melting method. The specific technology can be referred in reference [17]. The luminescent spectra were measured using a fluorescence spectrophotometer (F111AI). The excitation source is a xenon lamp (Xe900). The visible light was detected by a photomultiplier tube detector (PMTH-S1-R928).

Results and discussion

Under 975 nm excitation, the emission spectra of the Yb^{3+}/Er^{3+} co-doped phosphate glass ceramic at different temperatures had been studied. Fig. 1 is emission spectra of the Yb^{3+}/Er^{3+} co-doped phosphate glass ceramic in the 500–600 nm wavelength region at 295 K and 635 K. The green up-conversion emissions at 523 nm and 550 nm should come from the transitions of Er^{3+} ions: $^2H_{11/2}$-$^4I_{15/2}$ and $^4S_{3/2}$-$^4I_{15/2}$, respectively. With increasing of the sample temperature, the intensity of the green up-conversion emission at 550 nm decreases, but the intensity of the green up-conversion emission at 523 nm increases gradually. The positions of the two emission bands do not change with increasing of sample temperature, which shows the energy gap between $^2H_{11/2}$ and $^4S_{3/2}$ levels almost keeps unchanged. The intensities of the two green

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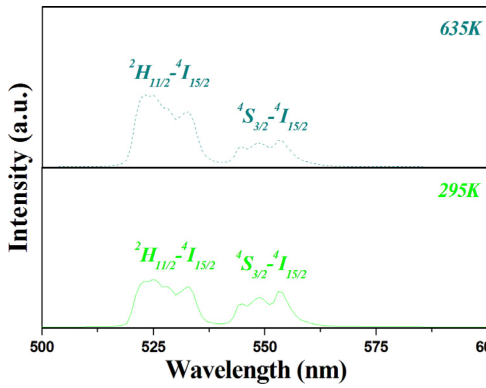

Fig. 1. Emission spectra of the Yb^{3+}/Er^{3+} co-doped phosphate glass ceramic at 295 K and 635 K under 975 nm excitation.

emissions can vary with the temperature, which indicates the heat has affected the populations of $^2H_{11/2}$ and $^4S_{3/2}$ levels. Considering the small energy gap between $^2H_{11/2}$ and $^4S_{3/2}$, with a value of ~500 cm^{-1} estimated from the emission spectra, the relative population of two levels should follow a Boltzmann-type population distribution. The luminescent intensity ratio of two upconversion green emissions can be described as Eq. (1).

$$R \equiv \frac{I_H}{I_S} = \frac{N(^2H_{11/2})}{N(^4S_{3/2})} = \frac{g_H \sigma_H \omega_H}{g_S \sigma_S \omega_S} \mathrm{Exp}\left(\frac{-\Delta E}{kT}\right) = \mathrm{CExp}\left(\frac{-\Delta E}{kT}\right) \quad (1)$$

where N, g, σ, ω are the population number, the degeneracy, the emission cross-section, and the angular frequency of the two green emissions, ΔE is the energy gap between the $^2H_{11/2}$ and $^4S_{3/2}$ levels, T is the absolute temperature of the sample, The pre-exponential constant is given by $C = g_H\sigma_H\omega_H/g_S\sigma_S\omega_S$.

Fig. 2 is a mono-log plot of the luminescent intensity ratio of the two green emissions as a function of inverse absolute temperature in the range from 295 K to 635 K. The experimental data can be fitted by straight line, whose slope is ~1110.2. The sensor sensitivity can be defined as Eq. (2).

$$dR/dT = R\left(-\frac{\Delta E}{kT^2}\right) \quad (2)$$

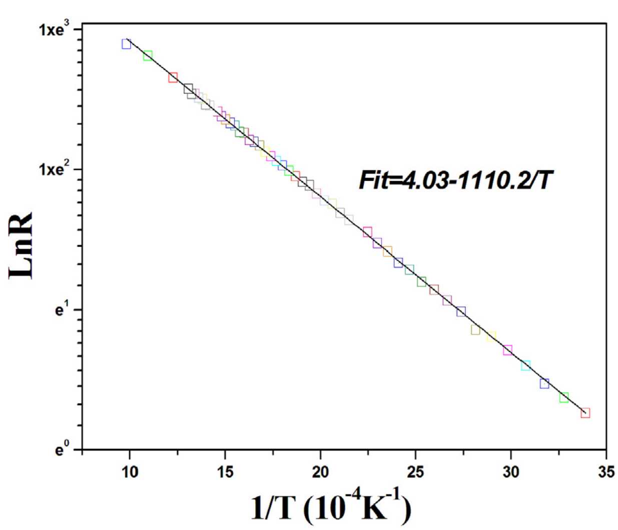

Fig. 2. Mono-log plot of the FIR as a function of inverse absolute temperature.

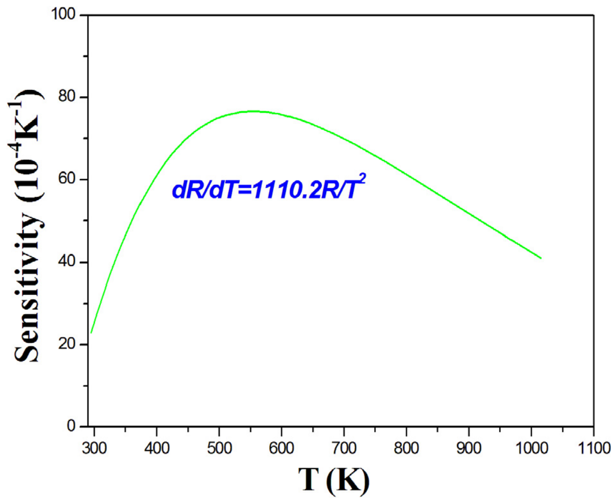

Fig. 3. Sensor sensitivity as a function of the temperature.

The corresponding resultant curve is shown in Fig. 3. The sensitivity of Er^{3+}/Yb^{3+} co-doped phosphate glass ceramic reached the maximal value of ~0.0077 K^{-1}. The sensitivity is relatively flat at the high temperature region.

Conclusions

By high-temperature melting method and thermal annealing technology, Yb^{3+}/Er^{3+} co-doped phosphate glass ceramic was prepared to explore fluorescence temperature sensor. The luminescent spectra of the sample in the 500–600 nm wavelength region were measured under 975 nm excitation. The strong green upconversion emissions, coming from the transitions of Er^{3+} ion: $^2H_{11/2}$-$^4I_{15/2}$ and $^4S_{3/2}$-$^4I_{15/2}$, were observed. The fluorescence intensity ratio can change with the increasing of temperature. The sensitivity of Er^{3+}/Yb^{3+} co-doped phosphate glass ceramic reached the maximal value of ~0.0077 K^{-1}. The sensitivity is relatively flat at the high temperature region. The Yb^{3+}/Er^{3+} co-doped phosphate glass ceramic will be valuable to applying to fluorescence temperature sensor.

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