

Green Upconversion Emission of Yb³⁺/Er³⁺ co-doped Gd₂Sn₂O₇

Nanophosphors as Wide-range Temperature Sensor

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Abstract. Gd₂Sn₂O₇:Yb³⁺/Er³⁺ (abbreviation for GSO: Yb³⁺/Er³⁺) nanophosphors codoped with Er³⁺ (0.1-2 at%) and Yb³⁺ (0.5-5 at%) were synthesized by a microwave hydrothermal process and annealed at 800 °C for 5 h. Powder X-ray diffraction, field emission scanning electron microscopy, transmission electron microscopy and upconversion emission spectra were used to characterize the as-synthesized sample. Under the irradiation of 980 nm laser diode, the GSO: Yb³⁺/Er³⁺ nanophosphors emitted green emissions centered at 525 and 546 nm (Er³⁺: ²H_{11/2}→⁴I_{15/2} and ⁴S_{3/2}→⁴I_{15/2} transition), red emissions centered at 659 and 677 nm (Er³⁺: ⁴F_{9/2}→⁴I_{15/2} transition). The temperature dependent emission intensity ratio of the thermally coupled levels (²H_{11/2}/⁴S_{3/2}) of Er³⁺ in the wide-range of 110-573 K was recorded to study the optical thermometric properties of GSO: Yb³⁺/Er³⁺ nanophosphors. The maximum sensitivity of GSO: Yb³⁺/Er³⁺ nanophosphors was approximately 36.34×10⁻⁴ K⁻¹ at 466 K. This result indicates that GSO: Yb³⁺/Er³⁺ nanophosphors are potential candidates for wide-range optical temperature sensors with high sensitivity.

Keywords: Luminescence; Microwave hydrothermal method; Upconversion; Temperature sensing.

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1 Introduction

Temperature is an important and fundamental physical parameter in science, engineering and industry, which can be accurately measured by different methods. Conventional contact temperature measurement is one of effective methods to study some phenomena with temperature. However, it is difficult to measure the temperature directly in some fields, such as high-voltage power stations, coal mines, corrosive circumstances and biocompatible temperature probe.¹⁻⁶ Compared with contact temperature measurement, the non-invasive optical temperature sensor, which is based on the UC emissions of rare earth (RE)-doped materials using a fluorescence intensity ratio (FIR) technique, has been widely investigated owing to its high resolution, fast response and independence of the measurement conditions.^{7,8} Over the last few years, some impressive achievements have been obtained in optical temperature sensors.⁹⁻¹² The Yb³⁺/Er³⁺-codoped NaYF₄ nanoparticles can be operated in the temperature range of 160-300 K with a maximum sensitivity of ~0.0012 K⁻¹.¹³ Furthermore, it was revealed that the optical temperature sensor which is based on Er³⁺-doped fluorotellurite glass can be manipulated in the temperature range of 330-550 K.¹⁴ Note that, these temperature sensors can be operated only at either high temperature or low temperature, suggesting that high- and low-temperature thermometry cannot be simultaneously realized in single sensor, which limits their further

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applications. Therefore, finding an efficient temperature sensor which can be simultaneously realized in high- and low-temperature thermometry is very imperative.

The series of stannates pyrochlore oxides ($A_2Sn_2O_7$ $A=Y, La, Gd$) with interesting optical, electrical and magnetic properties, have attracted considerable attentions owing to its potential applications including display, high temperature pigments, piezoelectricity, giant magnetic resistance, and so on.¹⁵⁻²⁰ More importantly, the low cut-off phonon energy of pyrochlore compounds ($Gd_2Sn_2O_7 < 610\text{ cm}^{-1}$)²¹, which will help decrease the nonradiative transition probability and increase the quantum yield of luminescence. In addition, pyrochlore compounds possess high thermal and chemical stability as well as wide optical band gap (3.7 eV). Nevertheless, to the best of our knowledge, there is no report on green UC emission and optical sensing behavior of GSO: Yb^{3+}/Er^{3+} nanophosphors.

In this paper, GSO: Yb^{3+}/Er^{3+} nanophosphors were successfully synthesized by microwave hydrothermal method with further heat treatment. The UC luminescence properties of GSO: Yb^{3+}/Er^{3+} nanophosphors are investigated in detail by varying doping concentrations of Yb^{3+} (and Er^{3+}) ions in the host. Furthermore, the temperature sensing behavior of the obtained GSO: Yb^{3+}/Er^{3+} nanophosphors was also investigated using the FIR technique for high- and low-temperature thermometry.

2 Experimental

2.1 Preparation of samples

The GSO: Yb^{3+}/Er^{3+} nanophosphors with different Yb^{3+} (Er^{3+}) doping concentration were prepared by microwave hydrothermal method followed by further calcining treatment²². $SnCl_4 \cdot 5H_2O$ (AR), ytterbium oxide (Yb_2O_3 , 99.99%), erbium oxide (Er_2O_3 , 99.99%), gadolinium oxide (Gd_2O_3 , 99.99%), HNO_3 and $NaOH$ were used as the starting materials without any further purification. A procedure synthesis for GSO: Yb^{3+}/Er^{3+} (Yb^{3+} 4 at%; Er^{3+} 0.5 at%) sample as a typical example is described as follows: Firstly, 0.0158 g Yb_2O_3 , 0.0019 g Er_2O_3 and 0.3462 g Gd_2O_3 were first dissolved in dilute HNO_3 under heating (about 120 °C). After the Yb_2O_3 , Er_2O_3 and Gd_2O_3 were completely dissolved. Then deionized water was added to obtain $Yb(NO_3)_3$, $Er(NO_3)_3$ and $Gd(NO_3)_3$ solution. At the same time, 0.7012 g $SnCl_4 \cdot 5H_2O$ was also dissolved in

deionized water and added dropwise into the above solution with stirring. After a well-controlled amount of NaOH solution were added to the solution to pH=8 with vigorously stirring, a slurry-like white precipitation was formed. The precipitation was maintained under stirring for 2 h at room temperature and transferred into a glass vessel of 35 mL capacity and sealed. Then the glass vessel was placed in the cavity of a CEM Discover microwave using single mode and continuous power at 2.45 GHz. The temperature was ramped from room temperature to 200 °C in 10 min. The time (1 h), pressure (200 psi), and power (100 W) were computer controlled. The precursors were formed after the precipitates were washed with alcohol and deionized water three times and dried at 80 °C for 10 h. Finally, the precursors were annealed at 800 °C for 5 h in air to obtain final product. To investigate the effect of Yb³⁺ (Er³⁺) content on the luminescence intensity, the other phosphor samples with different Yb³⁺ (Er³⁺)-doped concentration were prepared by the same procedure.

2.2 Characterization of samples

Powder X-ray diffraction (XRD) patterns were performed on a Brucker D8-advance X-ray diffractometer using Cu-K α_1 radiation (40 kV, 40mA, $\lambda=0.15406$ nm). All the patterns were recorded from 2θ 15° to 75° with a step size of 0.02°. The morphology of the nanocrystals was characterized by a JSM6700F scanning electron microscope (SEM). Transmission electron microscope (TEM) measurements were carried out on a JEOL-2010 field emission transmission electron microscope. In order to investigate the temperature dependence of the UC emission, the sample was placed in a temperature-controlled copper cylinder, and its temperature was increased from 110 to 573 K. The UC spectra of sample at various temperatures were obtained using a Horiba/Jobin Yvon Fluorolog-3 double monochromator equipped with a Hamamatsu R928 Photomultiplier under the excitation of a 980nm diode laser with 150 mW and the excitation power density was about 3W/cm². The spectral resolution of the experimental set-up was 0.1 nm.

3 Results and discussion

3.1 Structure and morphology

The crystallinity and phase purity of the resultant samples are determined by means of the XRD technique. Fig. 1 shows XRD patterns of the Yb³⁺/Er³⁺-codoped GSO sample for (a) various Er³⁺

concentrations up to 2 at% with a fixed 4 at% Yb^{3+} and (b) various Yb^{3+} concentrations up to 5 at% with a fixed 0.5 at% Er^{3+} . As demonstrated, all the peak positions of the studied samples coincide well with those of the standard GSO (JCPDS NO.13-0186) in pyrochlore structure, implying that the prepared samples possessed a pure cubic phase and the dopants (Yb^{3+} and Er^{3+}) were successfully incorporated into the site of Gd^{3+} ions of GSO host lattices without inducing any impure phases. It is noted that the diffraction peak (222) of $\text{GSO}:\text{Yb}^{3+}/\text{Er}^{3+}$ samples slightly shift to the high angles with the addition of Yb^{3+} and Er^{3+} ions, since the radii of Yb^{3+} (0.099 nm) and Er^{3+} (0.100 nm) are slightly smaller than that of Gd^{3+} (0.102 nm). We conclude that Yb^{3+} and Er^{3+} have been efficiently incorporated into the host lattice of GSO crystal.

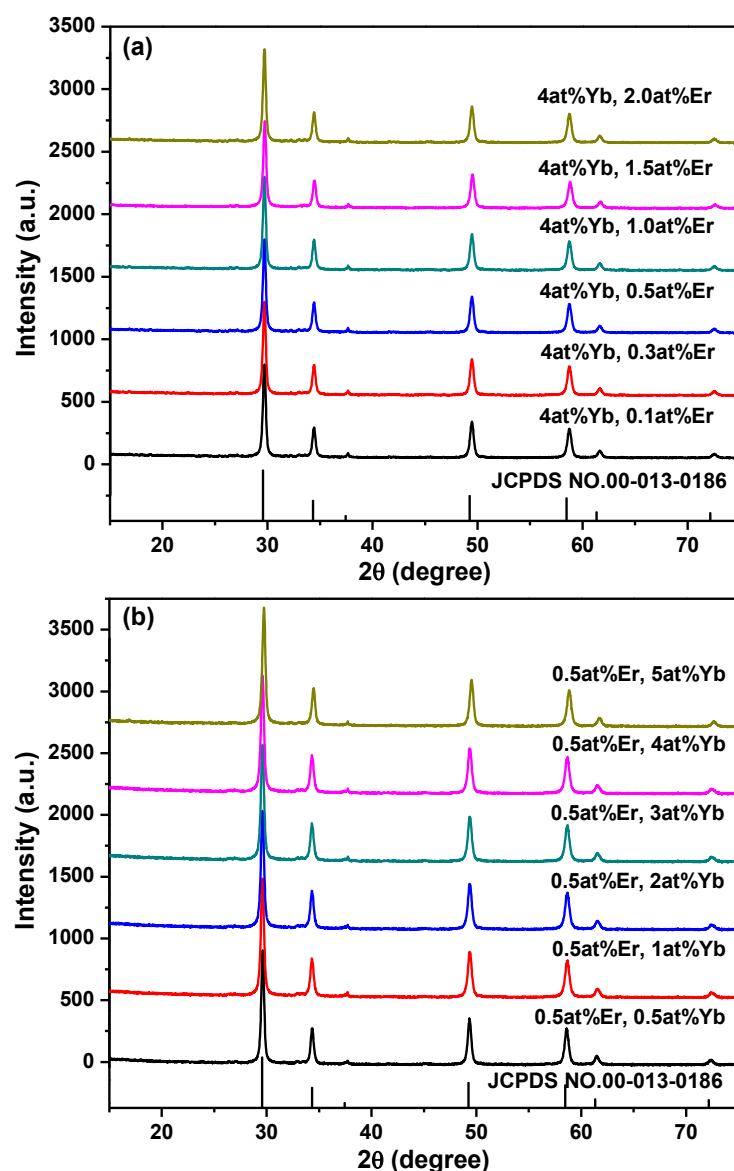


Fig.1 XRD patterns for GSO:Yb³⁺/Er³⁺ with (a) Er³⁺ concentration from 0.1 to 2 at% with a fixed 4 at% Yb samples and (b) Yb³⁺ concentration from 0.5 to 5 at% with a fixed 0.5 at% Er. The standard data for Gd₂Sn₂O₇ (JCPDS NO.13-0186) is also presented in the figure.

The morphological and particle size of the synthesized compounds were characterized by using SEM and TEM. The SEM image of the GSO:Yb³⁺/Er³⁺ samples (Yb³⁺ 4 at%; Er³⁺ 0.5 at%) presented in Figure 2a reveals that the morphology is rice-like nanoparticles with the average size of about 100 nm. Moreover, the TEM image shown in Fig. 2b also indicate that the GSO:Yb³⁺/Er³⁺ sample consist of aggregated nanoparticles. The selected area electron diffraction (SAED) pattern from GSO:Yb³⁺/Er³⁺ sample exhibited bright dots (see Fig. 2c), indicating that the samples were single crystalline in nature. Combining with the high-resolution TEM (HR-TEM) image (see Fig. 2d), the clear lattice fringe of GSO:Yb³⁺/Er³⁺ sample displays interplanar spacing of 0.303 nm in the particle, which is in well accordance with that of the (222) plane of the pyrochlore structure GSO crystal. This result suggests that high quality cubic GSO nanocrystals are formed. The above results indicated that the GSO:Yb³⁺/Er³⁺ nanocrystals can be successfully obtained by MH method.

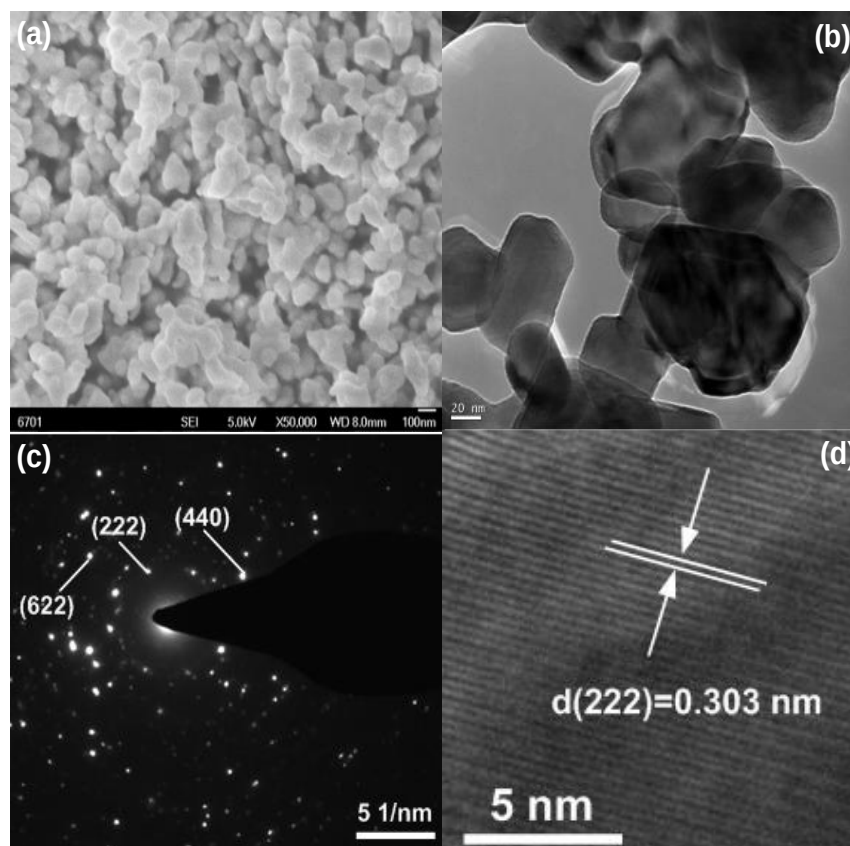


Fig. 2 (a) SEM image of the GSO:4 at%Yb³⁺, 0.5 at%Er³⁺ sample; (b) TEM image of GSO:Yb³⁺/Er³⁺ sample; (c) SAED spectrum of GSO:Yb³⁺/Er³⁺ sample; (d) HRTEM image of GSO:Yb³⁺/Er³⁺ sample.

3.2 UC luminescence studies

To analyze the effect of Yb³⁺ and Er³⁺ concentrations on the UC emission behaviors of GSO:Yb³⁺/Er³⁺, Fig. 3a and Fig. 3b show the dependence of the UC luminescence spectra of the GSO:Yb³⁺/Er³⁺ phosphors on the sensitizer (Yb³⁺) and activator (Er³⁺) concentrations, respectively. Upon 980 nm laser diode excitation, it is evident that all the samples consist of three emission bands in the visible region. The two green emissions located at 525 nm and 546 nm can be attributed to ²H_{11/2}→⁴I_{15/2} and ⁴S_{3/2}→⁴I_{15/2} transitions of Er³⁺ ion, respectively. The one red emission is located at 677 nm, can be attributed to ⁴F_{9/2}→⁴I_{15/2} transition of the Er³⁺ ion. When the concentrations of Yb³⁺ are fixed at 4 at%, the green and red emission intensity becomes more intense with the increasing of Er³⁺ content and reaches its optimum value (0.5 at%), and then quenching occurred with further increase of the dopant concentration (see Fig. 3a). With the increase of the Er³⁺ concentration, the average distance between Er³⁺ ions become shorter and the energy transfer become convenient.²³ Considering the luminescence quenching process often attributes to the energy transfer within the rare earth ion, the critical distance (R_c) can be calculated in terms of the equation²⁴: $R_c = 2 \left(\frac{3V}{4\pi NX_c} \right)^{1/3}$ where V is the volume of the unit cell, N is the number of available crystallographic sites occupied by the activator ions in the unit cell and X_c is the critical concentration. The values of V and N for the crystalline GSO (cubic system, $a=b=c=1.046$ nm, $Z=1$, $V=abc$, $N=Z$) are 1.144 nm^3 and 1, respectively.²⁵ Considering the above optimum concentration as the critical concentration X_c , the R_c for Er³⁺ is 7.5884 nm in the Gd_{0.955}Yb_{0.04}Er_{0.005}Sn₂O₇ phosphor. In addition, as the concentrations of Er³⁺ are fixed at 0.5 at%, the green and red UC emission intensity become stronger with the raising of Yb³⁺ content and reaches its optimum value (4 at%), which is demonstrated in Fig. 3b. The luminescence quenching leads to intensity decreasing as the concentration of Yb³⁺ over 4 at%. This is believed to be due to the onset of the quenching effect that self-quenching and the excitation of Er³⁺ energy back transfers to Yb³⁺ in high-Yb³⁺ doping concentration.^{26,27}

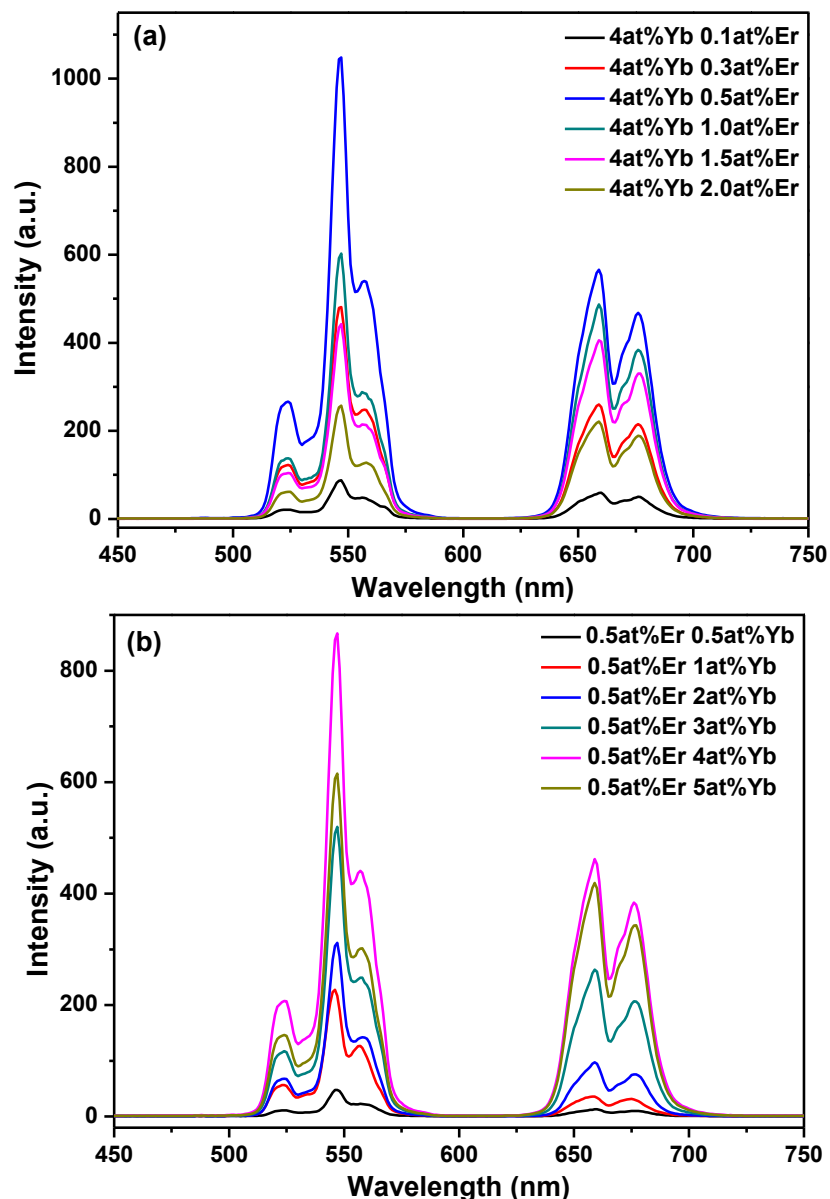


Fig. 3 UC emission spectra of the GSO:Yb³⁺/Er³⁺ samples for (a) different Er³⁺ concentration a fixed 4 at% Yb³⁺ and (b) different Yb³⁺ concentration with a fixed 0.5 at% Er under 980 nm excitation.

To better expound the UC luminescence mechanism, the power dependent UC emission spectra were measured (see Fig. 4a). We can determine the excitation power (P) versus UC emission intensity (I) dependence curve (see Fig. 4b). The details for dependences of UC emission intensities on pump power theory can be found in Ref..²⁸ The obtained results indicate that the population of the ²H_{11/2}, ⁴S_{3/2} and ⁴F_{9/2} emitting levels originate from two-photon process.³¹

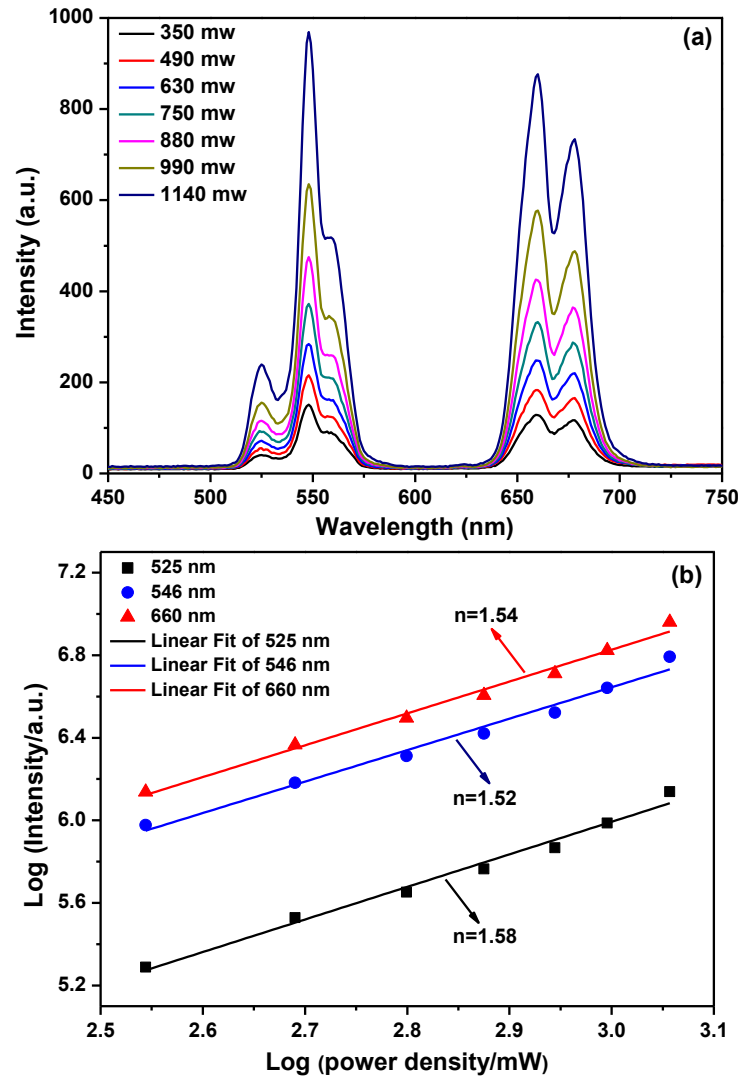


Figure 4. (a) The UC emissions spectra and (b) dependences of the UC intensities (I_{em}) of $(^2H_{11/2}, ^4S_{3/2}) \rightarrow ^4I_{15/2}$ and $^4F_{9/2} \rightarrow ^4I_{15/2}$ transitions on the 980 nm pumping laser power (I_p) for GSO:Yb³⁺/Er³⁺ phosphors.

Figure 5 displays the simplified energy level of Yb³⁺ and Er³⁺ ions as well as the proposed UC mechanism of Yb³⁺/Er³⁺-codoped GSO. Under 980 nm excitation, the Yb³⁺ at the ground $^2F_{7/2}$ state are firstly excited to the $^2F_{5/2}$ level. Then Yb³⁺ ions at $^2F_{5/2}$ excited state non-radiatively relax to $^2F_{7/2}$ state, transferring the energy to the adjacent Er³⁺ ion at $^4I_{15/2}$ ground level. This energy transfer process promotes Er³⁺ ion to $^4I_{11/2}$ excited state. This process can be described as ET1: $^2F_{5/2} (Yb^{3+}) + ^4I_{15/2} (Er^{3+}) \rightarrow ^2F_{7/2} (Yb^{3+}) + ^4I_{11/2} (Er^{3+})$. Subsequently, Er³⁺ ions at $^4I_{11/2}$ excited state are further populated to $^4F_{7/2}$ states by ET2 process: $^2F_{5/2} (Yb^{3+}) + ^4I_{11/2} (Er^{3+}) \rightarrow ^2F_{7/2} (Yb^{3+}) + ^4F_{7/2} (Er^{3+})$. Afterwards, these Er³⁺ ions at $^4F_{7/2}$ excited state nonradiatively relax to the $^2H_{11/2}$ and $^4S_{3/2}$ green-emitting state and further radiatively relax down the ground state $^4I_{15/2}$ to produce green emissions at 525 and 546 nm, respectively. For red emission ($^4F_{9/2} \rightarrow ^4I_{15/2}$), $^4F_{9/2}$

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emitting level of Er^{3+} ions can be pumped by two ways: (1) nonradiatively relaxation from the $^4\text{S}_{3/2}$ levels; (2) ET3 process: $^2\text{F}_{5/2}(\text{Yb}^{3+}) + ^4\text{I}_{13/2}(\text{Er}^{3+}) \rightarrow ^2\text{F}_{7/2}(\text{Yb}^{3+}) + ^4\text{F}_{9/2}(\text{Er}^{3+})$.²⁸⁻³¹

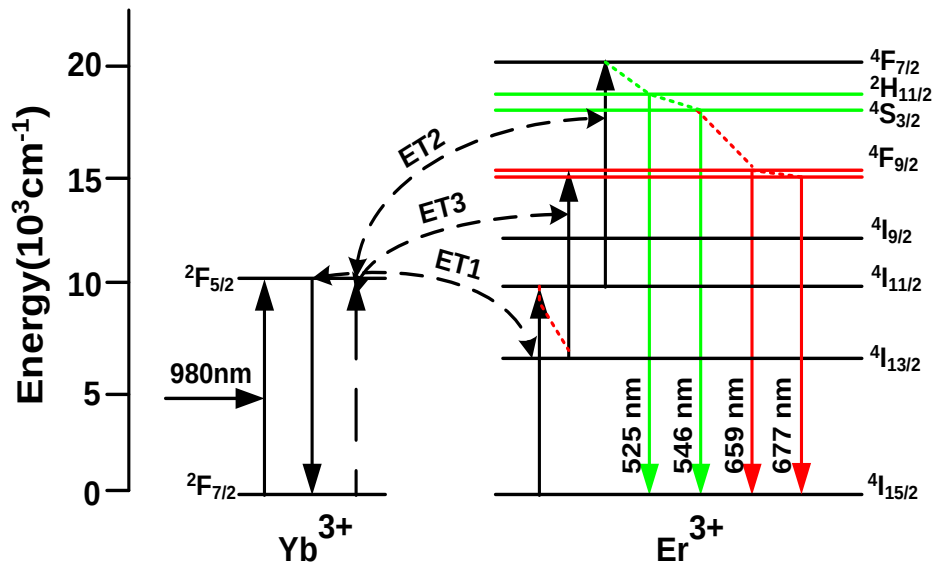


Figure 5. Energy level diagrams of Yb^{3+} and Er^{3+} ions and UC emission mechanism in $\text{GSO}:\text{Yb}^{3+}/\text{Er}^{3+}$ phosphors.

3.3 Optical temperature sensing behavior

To explore the optical thermometric properties of the studied samples, the green UC emission spectra of $\text{GSO}:4 \text{ at\% } \text{Yb}^{3+}/0.5 \text{ at\% } \text{Er}^{3+}$ phosphor as a function of temperature (range from 110 to 573 K) were measured and shown in Fig. 6, in which the spectra are normalized to the emission peak at 546 nm. It is clearly seen that the green emission peak positions are no remarkable shift while the fluorescence intensity ratio (FIR) of green UC emission from $^2\text{H}_{11/2} \rightarrow ^4\text{I}_{15/2}$ to $^4\text{S}_{3/2} \rightarrow ^4\text{I}_{15/2}$ increase with the rise of temperature. According to previous reports, the relative population of the thermally coupled energy levels follows the Boltzmann distribution and the FIR of two green UC emissions can be defined as [23]:

$$FIR = \frac{I_1}{I_2} = \frac{n_1}{n_2} = \frac{g_1 \omega_1 \delta_1}{g_2 \omega_2 \delta_2} \exp\left(\frac{-\Delta E}{kT}\right) = B \exp\left(\frac{-\Delta E}{kT}\right) \quad (1)$$

where I_1 and I_2 demonstrate the integrated green UC emission intensities for the thermally coupled levels $^2\text{H}_{11/2} \rightarrow ^4\text{I}_{15/2}$ and $^4\text{S}_{3/2} \rightarrow ^4\text{I}_{15/2}$ transitions, respectively. In general, n , g , ω , δ represent the number of ions, the degeneracy, the angular frequency, the emission cross section of fluorescence transitions from excited state ($^2\text{H}_{11/2}$ and $^4\text{S}_{3/2}$) to the ground state ($^4\text{I}_{15/2}$), respectively. ΔE is the energy gap between the $^2\text{H}_{11/2}$ and $^4\text{S}_{3/2}$ levels, k is the Boltzmann coefficient, B presents the pre-exponential factor and T is the absolute temperature.

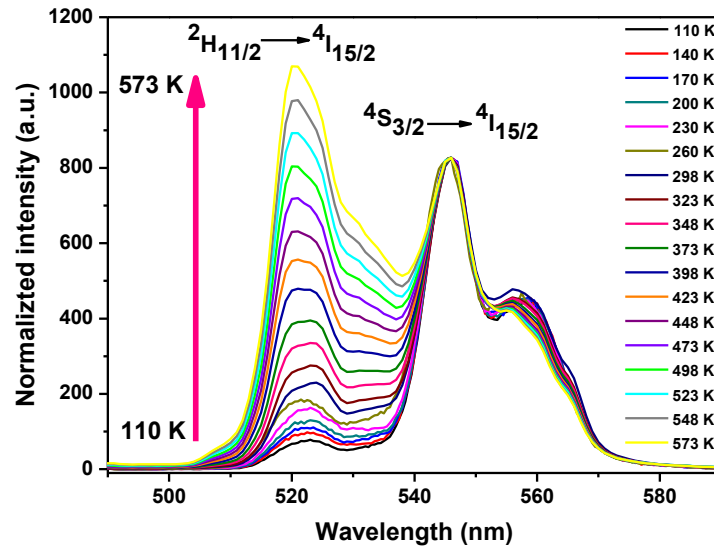


Figure 6. Temperature dependence of the green UC luminescence spectra of GSO:Yb³⁺/Er³⁺ phosphor under 980 nm excitation (the spectra are normalized to the emission peak at 546 nm. The excitation power density is 3W/cm²). The temperature dependence of the fluorescent intensity ratio (FIR) value from 110 to 573 K for GSO:4 at% Yb³⁺/0.5 at% Er³⁺ phosphor was calculated and displayed in Fig. 7a. According to the Equ. (1), the value of Ln(FIR) versus the inverse absolute temperature (1/T) is plotted in Fig. 7b. The linear fitting of the experimental data gave slope ($\ln B$) and intercept ($\Delta E/k$) equal to 1.83 and 932.49, respectively. As a consequence, the pre-exponential factor and the energy gap ΔE are evaluated to be about 6.23 and 647 cm⁻¹, respectively. The fitted energy gap ΔE is very close to the previous reports (about 700 cm⁻¹).³²

For thermometers, sensor sensitivity is a very important parameter to illustrate the temperature sensing ability. According to previous literature, the sensitivity (S) of temperature detection can be defined by the following formula²⁷:

$$S = \frac{dFIR}{dT} = FIR \left(\frac{\Delta E}{kT^2} \right) = B \left(\frac{\Delta E}{kT^2} \right) \exp \left(-\frac{\Delta E}{kT} \right) \quad (2)$$

By means of Equ. (2), the calculated curve of sensor sensitivity as a function of absolute temperature is shown in Fig. 7c. It can be clearly found that the sensitivity keeps increasing, achieves its maximum value of $36.34 \times 10^{-4} \text{ K}^{-1}$ at 466 K and then decreases with further increase of temperature. Generally, we consider that when the sensitivity S is higher than half of its maximum value $S_{\max}$, the temperature sensing result is reliable.³³ As can be seen from Fig. 7c,

the GSO:Yb³⁺/Er³⁺ phosphor has large temperature sensing region locating between 110 K and 573 K for green emission, which is beneficial to the practical applications.

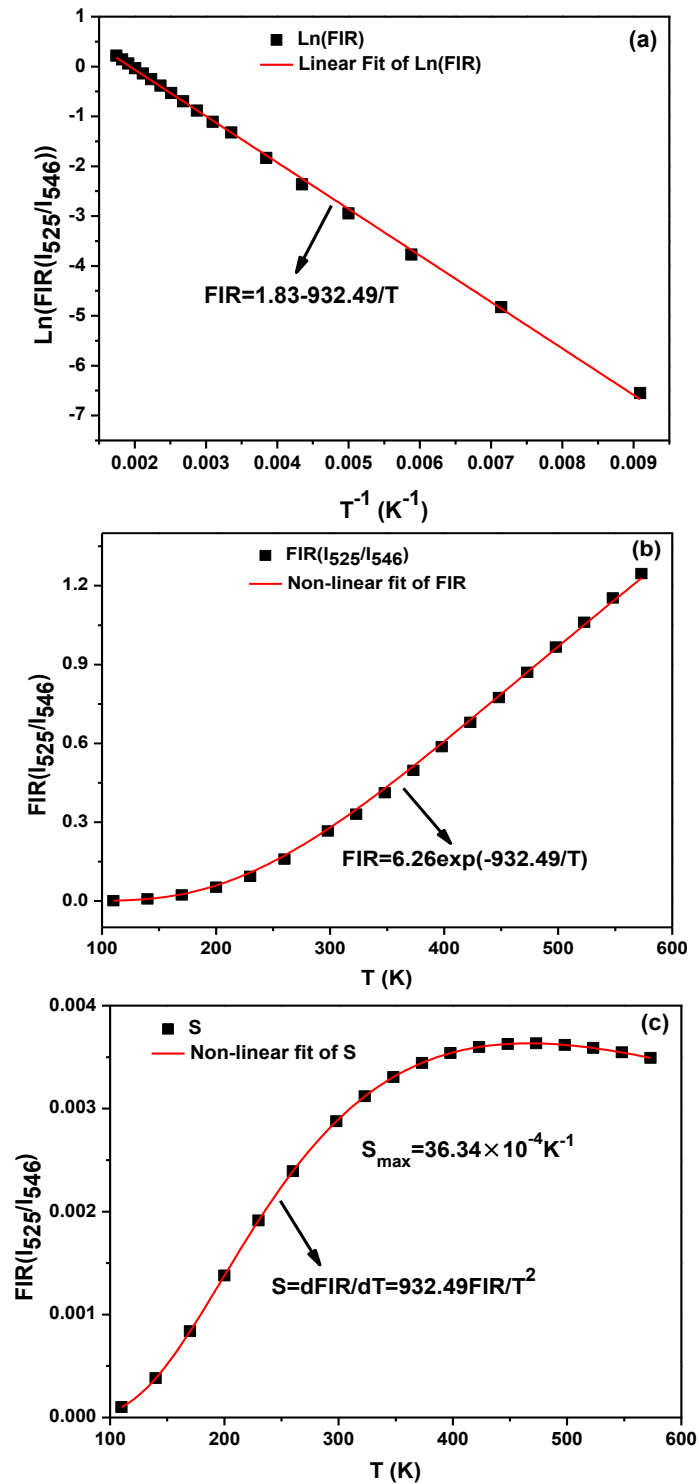


Figure 7. The green UC emission-based temperature-sensing behaviour of GSO:Yb³⁺/Er³⁺ phosphor: (a) monolog plot of the FIR as a function of the inverse absolute temperature; (b) FIR relative to the temperature; (c) sensor sensitivity as a function of temperature.

4 Conclusions

We synthesized the GSO:Yb³⁺/Er³⁺ phosphors by a MH method for optical temperature sensing applications. The intense visible UC luminescence of sample is clearly observed under 980 nm excitation. The transition mechanisms of the UC luminescence can be ascribed to a two-photon absorption process. The optimum doping concentration of GSO for UC emission is about 4 at% Yb³⁺ and 0.5 at% Er³⁺. Under the excitation of 980 nm, the green UC emissions at 525 nm (²H_{11/2}→⁴I_{15/2}) and 546 nm (⁴S_{3/2}→⁴I_{15/2}) have been utilized for optical thermometry via the fluorescence intensity ratio technique. The dependence of FIR for the sample GSO:4 at% Yb³⁺/0.5 at% Er³⁺ with optimal composition on temperature were measured in the wide range of 110-573 K, and the sensitivities of sample reach the maximum 36.34×10⁻⁴ K⁻¹ at 466 K for green emission. These results are expected to provide a deep insight into the GSO:Yb³⁺/Er³⁺ nanophosphors for applications in wide-range optical temperature sensors.

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