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Optical thermometry through infrared excited green upconversion in monoclinic phase $Gd_2(MoO_4)_3$:Yb^{3+}/Er^{3+} phosphor

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ABSTRACT

Monoclinic phase $Gd_2(MoO_4)_3$: Yb^{3+}/Er^{3+} phosphor is synthesized via a simple sol-gel method. The XRD result reveals that the phosphor possesses monoclinic structure with space group *C*2/*c*(15). Under the excitation of a 980 nm laser, its emission spectra shows remarkably intense green and negligible red emissions, which are all two-photon process. By investigating effect of temperature on green emission of the sample, the competition between the thermal agitation and non-radiative relaxation of $^2H_{11/2}$ level can be found, which is verified by the measurement of lifetime. In addition, the sensitivity of optical thermometry is studied based on the fluorescence intensity ratio technique through infrared excited green upconversion. The maximum sensitivity is found to be about 0.02574 K^{-1} at 510.2 K, suggesting that the phosphor can be used as an excellent material for optical temperature sensing.

1. Introduction

In recent years, the optical temperature sensing based on the upconversion (UC) [1] emission attracted much attention for high sensitivity and accuracy. Compared with the traditional temperature sensors that base on the principle of expansion with heat and contraction with cold, optical thermometry of UC emission based on the fluorescence intensity ratio (FIR) technique has many unique advantages [2–6], such as noncontact measurement [7–9], high resolution and so on. Among the rare earths, Er^{3+} is considered to be one of preferably doped ion in optical thermometry via FIR technique. The $^2H_{11/2}$ and $^4S_{3/2}$ states of Er^{3+} satisfied with Boltzmann distribution [10] are the thermal coupling energy levels. Under the excitation of a 980 nm laser, Yb^{3+} has large absorption cross section and greatly efficient energy transfer from Yb^{3+} to Er^{3+} [11,12], so it is usually used as the co-doped ion to sensitize Er^{3+}.

It was reported that the optical temperature sensitivity of Yb^{3+}/Er^{3+} co-doped phosphor can be affected by some factors [13,14], such as excitation power density, doping concentration, phase structure, the size of sample, and so on. Hao et al. [13] reported that high Yb^{3+} concentration doped sample showed preferably optical sensitivity due to the energy back transition. Moreover, they also observed that the temperature of sample is ascended by a large value of 94 K when the excitation pump power density changes from 1.0 to 13.1 W cm^{-2}. Besides, Anurag et al. obtained that the intensity ratio of green and red emissions depends strongly on the excitation power density [2].

In order to obtain an excellent optical temperature sensing, the matrix is considered to be an importantly influencing factor [3,15]. It is known that the matrix of the optical temperature sensors mainly focused on the glass and fluoride materials at early time. However, the poor stability and toxicity properties of glass and fluoride materials greatly hinder their further applications [16]. $Gd_2(MoO_4)_3$ is possessed of stable chemical and thermal properties, moisture free and a low excitation threshold. Lower symmetry is conducive to the enhancement of crystal field. The rare-earth ions in a crystal field with lower symmetry are susceptible to be excited [17]. Thus, monoclinic phase $Gd_2(MoO_4)_3$ is more conducive to the enhancement of fluorescence compared with orthorhombic phase, making it to be a wise choice as the host matrix in optical thermometry.

In this work, the $Gd_2(MoO_4)_3$: Yb^{3+}/Er^{3+} phosphor is synthesized using a simple sol-gel method. The sample exhibits the strong green and relatively weak red emission under the excitation of a 980 nm laser. Furthermore, the dependences of UC luminescence,

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luminescence decay time and optical sensitivity on temperature are investigated.

2. Material preparation

$Gd_2(MoO_4)_3$ phosphors doped with 0.01 mol. % Er^{3+}, 0.09 mol. % Yb^{3+} are prepared by a simple sol-gel method. Firstly, $Yb(NO_3)_3 \cdot 6H_2O$, $Er(NO_3)_3 \cdot 6H_2O$, $Gd(NO_3)_3 \cdot 6H_2O$, $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ are dissolved in 50 ml distilled water and the citric acid as chelating agent is added to this solution with the mole ratio of cations to citric acid to be 1:1.5. Subsequently, the pH of the solution is adjusted to 7 by adding 10 mL ammonia solution. The solution is heated at 80 °C on a hot plate with continuous magnetic stirring for 30 min. After that, the wet gel is dried at 130 °C for 20 h. Subsequently, the mixture is transferred to the alumina crucible, annealing in a furnace at the calcination temperature of 630 °C for 2 h in air atmosphere with a heating rate of 10 °C/min. Finally, the mixture is cooled down to room temperature naturally.

The crystal structure of the sample is characterized by an X-ray diffractometer (XRD) (Empyrean, Panalytical, Netherlands) at a scanning rate of 4° min^{-1} in the range from 10° to 60° with Cu Ka radiation (λ=0.15406 nm). The emission spectra are recorded by using a Spectrometer (HORIBA Jobin Yvom iHR550). A 980 nm laser is purchased from Beijing Kipling Photoelectric technology Co., Ltd. Luminescence lifetimes upon 980 nm excitation are measured and decay curves are collected under the same system by using a pulsed laser with the pulse duration of 100 μs and a repetition frequency of 500 Hz. For the thermometry experiments, a heating stage (Linkam THMS 600) is employed to heat the sample, and the temperature is measured by the thermocouple. Scanning electron microscope (SEM) measurements are performed using a Hitachi, S-4800 SEM equipped with the energy dispersive X-ray (EDX) spectrum.

3. Results and discussions

Fig. 1 shows the XRD pattern of the $Gd_2(MoO_4)_3$ phosphor at the calcination temperature of 630 °C. All the diffraction peaks agree properly with the monoclinic $Gd_2(MoO_4)_3$ pattern of JCPDS card#25-0338 with space group $C2/c(15)$. The strongest peak detected at $2\theta = 28.217°$ is at the lattice plane (−221). No additional peaks of other phases are found, indicating that the Yb^{3+} and Er^{3+} ions have been well built into the $Gd_2(MoO_4)_3$ host lattice.

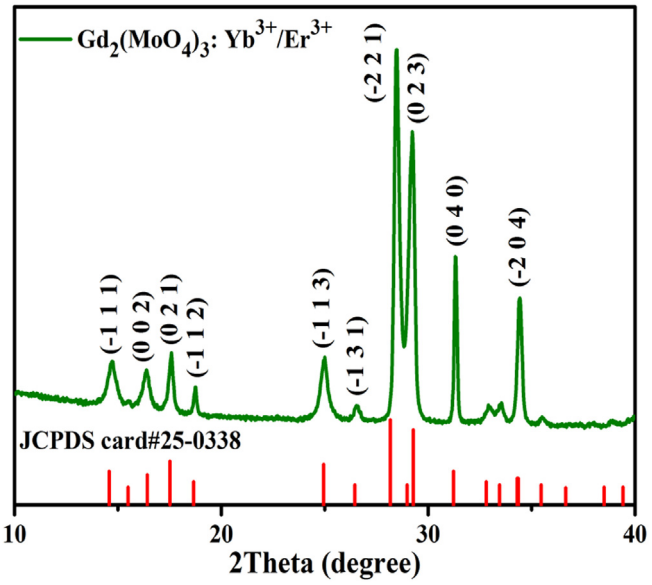

Fig. 1. X-ray diffraction (XRD) pattern of $Gd_2(MoO_4)_3$: Yb^{3+}/Er^{3+}phosphor annealed at 700 °C.

In order to study the morphology of the phosphor material, the scanning electron microscope (SEM) image of $Gd_2(MoO_4)_3$: Yb^{3+}/Er^{3+} phosphor annealed at 700 °C is shown in Fig. 2 (a). Morphology of the sample shows that the particles have irregular shapes. The energy dispersive X-ray spectroscopy (EDX) is also analyzed to investigate the chemical composition and purity of $Gd_2(MoO_4)_3$: Yb^{3+}/Er^{3+} phosphor. The EDX spectrum in Fig. 2 (b) confirms gadolinium (Gd), molybdenum (Mo), oxygen (O), ytterbium (Yb), and erbium (Er) elements in the sample.

The emission spectra of $Gd_2(MoO_4)_3$: Yb^{3+}/Er^{3+} phosphor under various excitation powers is shown in Fig. 3 (a), revealing remarkably intense green and relatively weak red emissions. Three emission peaks located around 530, 550 and 660 nm are found, which is assigned to the $^2H_{11/2} \rightarrow {}^4I_{15/2}$, $^4S_{3/2} \rightarrow {}^4I_{15/2}$ and $^4F_{9/2} \rightarrow {}^4I_{15/2}$ transitions of Er^{3+}, respectively. With increasing excitation power, the fluorescence peak position is almost unchanged but the emission intensity increases continuously. For unsaturated UC processes, the number of photons which are required to populate the emitting state can be obtained by the relation [18,19].

$$I \propto P^n \tag{1}$$

Where I is the fluorescent intensity, P is the pump power, and n is the number of photons required to populate the emitting state. In order to evaluate the number of photons which are involved in the luminescent mechanisms of the $Gd_2(MoO_4)_3$: Yb^{3+}/Er^{3+} phosphor, Fig. 3 (b) shows the dependence of the emission intensities on the excitation power, where the values of n are obtained to be 1.84, 1.60, 1.44 for 530, 550 and 660 nm, respectively. Thus, these emissions are two-photon process. Moreover, the thermal effect caused by the pump power cannot be avoided.

To study effect of temperature on green emission of $Gd_2(MoO_4)_3$:Yb^{3+}/Er^{3+} phosphor, Fig. 4 (a) shows the green emission spectra of $Gd_2(MoO_4)_3$:Yb^{3+}/Er^{3+} phosphor at different temperatures under the excitation of 79.0 mW/mm^2 pump power. All the emission peaks do not shift with increasing temperature. As shown in Fig. 4 (b), I_{530} (I_{530} is the integrated intensity corresponding to the $^2H_{11/2} \rightarrow {}^4I_{15/2}$ transition) increases gradually with increasing temperature from 298.6 to 345.2 K, then it decreases continuously with increasing temperature from 345.2 to 510.2 K. These results can be attributed to the competition between the thermal agitation and non-radiative relaxation of $^2H_{11/2}$ level [4,20]. Besides, I_{550} (I_{550} is the integrated intensity corresponding to the $^4S_{3/2} \rightarrow {}^4I_{15/2}$ transition) significantly decreases with increasing temperature from 298.6 to 510.2 K. From Fig. 4 (b), we can see that all green emission intensity decreases continuously as temperature increases. It is due to the aggravation of non-radiative relaxation with increasing temperature.

In order to investigate the effect of temperature on the luminescence dynamics of $^2H_{11/2}$ and $^4S_{3/2}$ states in Er^{3+}, we measure the luminescence decay curves of two green UC emission bands of Er^{3+} at different temperatures. The luminescence decay curves of Er^{3+} for the thermally coupled $^2H_{11/2}$ and $^4S_{3/2}$ states exhibit single exponential decay at different temperatures as shown in Fig. 5 (a) and (b). To calculate the lifetimes of the $^2H_{11/2}$ and $^4S_{3/2}$ states of Er^{3+} ions, a single exponential fitting is utilized by using the equation [21–23].