Journal of Luminescence 191 (2017) 13–17

Contents lists available at ScienceDirect

Journal of Luminescence

journal homepage: www.elsevier.com/locate/jlumin

Dual functions of Er^{3+}/Yb^{3+} codoped $Gd_2(MoO_4)_3$ phosphor: temperature sensor and optical heater

Hongyu Lu [a], Haoyue Hao [a], Yachen Gao [b], Guang Shi [a], Qiaodan Fan [a], Yinglin Song [a], Yuxiao Wang [a,*], Xueru Zhang [a,*]

[a] Department of Physics, Harbin Institute of Technology, Harbin 150001, China
[b] College of Electronic Engineering, Heilongjiang University, Harbin 150080, China

ARTICLE INFO

Article history:
Received 28 July 2016
Received in revised form
13 December 2016
Accepted 21 December 2016
Available online 23 December 2016

Keywords:
Temperature sensing
Fluorescence intensity ratio
Photo-thermal effect
Rare earth
Optical thermometer
Upconversion
Optical heater

ABSTRACT

$Gd_2(MoO_4)_3$:Er^{3+}/Yb^{3+} phosphor with respective functions of optical temperature sensing and optical heater are investigated in detail. The $Gd_2(MoO_4)_3$:Er^{3+}/Yb^{3+} film (~200 nm) and powder are successfully prepared, respectively. The crystalline structure is characterized by XRD and the relevant morphologies are analyzed by SEM and AFM, respectively. Based on fluorescence intensity ratio (FIR) technique, photo-thermal behaviors of $Gd_2(MoO_4)_3$:Er^{3+}/Yb^{3+} powder are illustrated. Under 980 nm excitation, the temperature induced by laser is calculated, which varies from 323 to 617 K as exciting power increased from 0.03 to 3.78 W. Additionally, the temperature sensing behaviors of $Gd_2(MoO_4)_3$:Er^{3+}/Yb^{3+} film are investigated. Highly accurate temperature sensing can be realized due to the negligible photo-thermal effect. This thermal sensor exhibited a high sensitivity in the range of 295–660 K, and the maximum value of relative sensitivity was determined as $13.4 \times 10^{-3}\ K^{-1}$ at 295 K. These results demonstrate that $Gd_2(MoO_4)_3$:Er^{3+}/Yb^{3+} phosphor can be applied in terms of temperature sensing and optical heater.

1. Introduction

Recently, lanthanide doped luminescent materials have been extensively investigated, due to their wide applications in many fields, such as optical temperature sensing, color display, bio-imaging and therapeutics [1–6]. Specially, comparing with conventional method of temperature measurement (thermocouple), optical thermometer is hardly affected by electromagnetic noise and corrosive environments [7]. Fluorescence intensity ratio (FIR) technique is a promising strategy to achieve accurate temperature sensing based on thermal equilibrium state between the thermal coupling levels, because it is independent of luminescence loss and fluctuations of excitation power [8–12]. Since green luminescence originating from $^2H_{11/2}$ and $^4S_{3/2}$ (thermal coupling level) to ground state are highly efficient, trivalent erbium (Er^{3+}) ion is regarded as one of the most excellent activator [13–15]. Vetrone et al. measured the intracellular temperature using $NaYF_4$:Er^{3+}/Yb^{3+} nanoparticle for the first time [16]. Sun et al. presented that the local structure around Er^{3+} ion significantly affect upconversion luminescence [17]. Therefore, appropriate matrix is a crucial factor for luminescent property. Among the candidates of host materials, due to low phonon energy and superior thermal stability, $Gd_2(MoO_4)_3$ has been marked as a very prominent host material [18–20].

Apart from temperature sensing, upconversion material is also considered as heater due to light-to-heat conversion ability [21–26]. It was recently reported that the laser-induced temperature increase can be up to ~10 °C for the cyclohexane dispersion of $NaGdF_4$:Yb^{3+}/Er^{3+} core-shell structures, and up to ~240 °C in solid powder state [27]. Tikhomirov et al. elucidated that the photo-thermal behavior of free-standing nanoparticles is stronger than bulk material which is attribute to confinement of phonons [28]. Jaque et al. achieved photo-thermal therapy and temperature sensing in vivo with LaF_3:Nd^{3+} nanoparticles [29]. The above mentions reflect the competition between upconversion luminescence (radiative) and photo thermal effect (nonradiative) in upconversion phosphor which represent a “dual function” (sensor and heater). However, photo-thermal effect is still an inevitable obstacle for optical temperature sensing.

Herein, we report a strategy to realize highly accurate temperate sensing using less photo-thermal film. The two forms of $Gd_2(MoO_4)_3$:Er^{3+}/Yb^{3+} phosphor (nanofilm and bulk material) are synthesized. Based on FIR technology, the photo-thermal behaviors are elucidated and the temperature induced by laser is calculated for powder phosphor. Meanwhile, in terms of film phosphor, the temperature sensing behavior is investigated.

* Corresponding authors.
E-mail addresses: wangyx@hit.edu.cn (Y. Wang), xrzhang@hit.edu.cn (X. Zhang).

http://dx.doi.org/10.1016/j.jlumin.2016.12.026
0022-2313/

2. Experimental

2.1. Preparation

For a typical synthesis of upconversion film, sol-gel method and spin-coating technique were used to prepare $Gd_2(MoO_4)_3$: 1%Er^{3+}/9%Yb^{3+} film. Firstly, an appropriate amount of $(NH_4)_6Mo_7O_{24}$ was dissolved in 15 mL 2-Methoxyethanol with 5 mL acetic acid glacial under constant magnetic stirring. Stoichiometric amounts of $Gd(NO_3)_3 \cdot 6H_2O$ (1.8 mmol), $Yb(NO_3)_3 \cdot 6H_2O$ (0.18 mmol) and $Er(NO_3)_3 \cdot 6H_2O$ (0.02 mmol) were dissolved in 10 mL of 2-Methoxyethanol and added dropwise. Subsequently, the citric acid (4.5 mmol) was added to this solution which acts as chelating agent of the metal ions, then a yellowish transparent solution was obtained after a few minutes. Finally, the sol was spin-coated on a quartz plate with a speed of about 3000 rpm for 60 s and heated to 60 °C for 8 h, and then it was preheated at 350 °C for 2 h and sintered at 800 °C for 2 h in air atmosphere. Under the same conditions, powder phosphor was also obtain.

2.2. Characterization

Upconversion luminescence spectrum were measured on HORIBA Jobin Yvon iHR550 Spectrometers which employs a photon-counting detection system using a photomultiplier tube. Powder X-ray diffraction (XRD) patterns were recorded by Panalytical Empyrean diffractometer. The thickness of the film was inspected by using FEI Helios Nanolab600i scanning electron microscope. The morphology of the crystalline film sample was inspected using Bruker Dimension FastScan atomic force microscope (AFM). The image of film photoluminescence was taken by Nikon Eclipse LV100POL Microscopes.

3. Results and discussion

The XRD patterns of the film and powder are shown in Fig. 1, which is in accord with the orthorhombic phase $Gd_2(MoO_4)_3$ (JCPDS No. 70-1397). Orthorhombic diffraction peak of film is observed except for the broad band (20–22°) [30], which is ascribed to a quartz glass substrate. The corresponding morphologies of film are recorded by SEM and AFM, as shown in Fig. 2(a) and (b), respectively. SEM image shows that the thickness of film is about 200 nm. The AFM image shows that the surface of film is very smooth with a R_a (roughness average) of 24 nm. The SEM image of powder phosphor reveals that the average particle size is 2 μm (Fig. 2(c)). The particles exhibit a tightly aggregation.

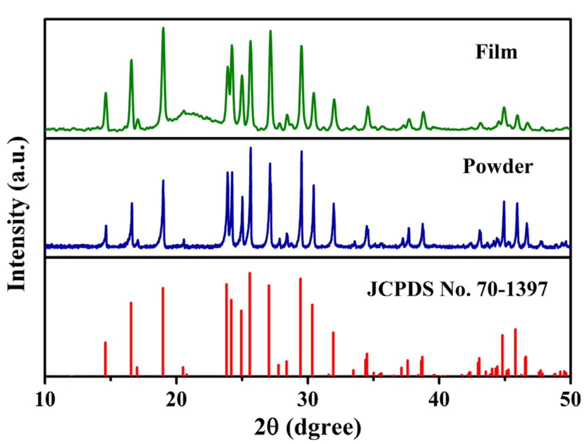

Fig. 1. XRD patterns of $Gd_2(MoO_4)_3$:Er^{3+}/Yb^{3+} film and powder phosphor with JCPDS No. 70-1397.

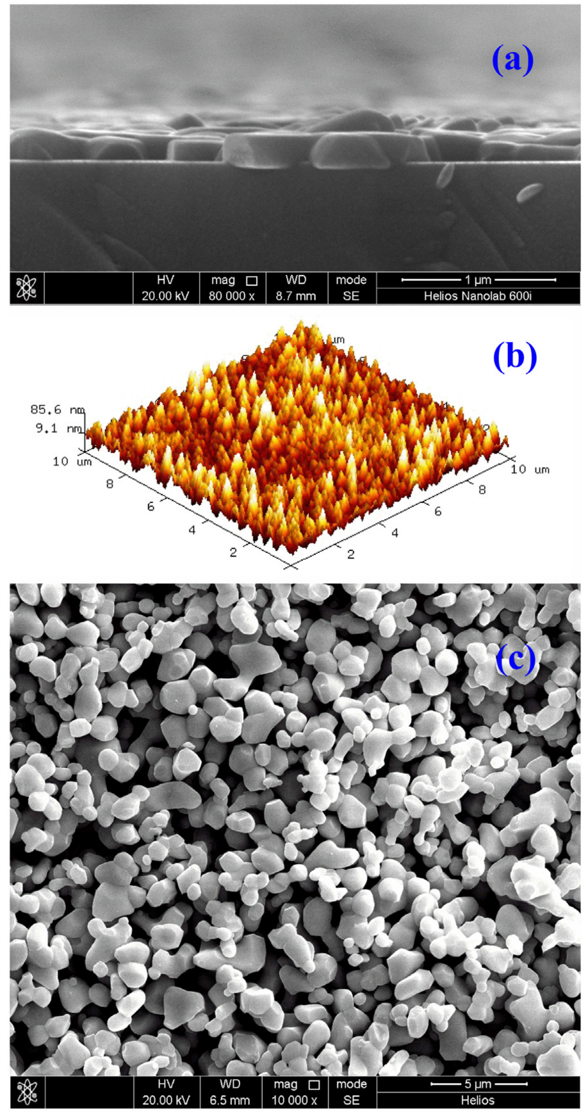

Fig. 2. (a) SEM image of $Gd_2(MoO_4)_3$:Er^{3+}/Yb^{3+} nanocrystal film; (b) AFM image of $Gd_2(MoO_4)_3$:Er^{3+}/Yb^{3+} nanocrystal film surface; (c) SEM image of $Gd_2(MoO_4)_3$:Er^{3+}/Yb^{3+} powder.

3.1. Photo-thermal behavior

Because relative populations of thermally coupled levels obey the Boltzmann distribution, the FIR can be represented as [31–33]:

$$FIR = \frac{I_H}{I_S} = \frac{g_H A_H \omega_H}{g_S A_S \omega_S} \exp\left(\frac{-\Delta E}{kT}\right) = C \exp\left(\frac{-\Delta E}{kT}\right) \tag{1}$$

where I_H and I_S represent the integral intensity of emission band, g $(=2J+1)$, A, ω are the degeneracy, the radiative transition probabilities, and the angular frequency of fluorescence transitions from the $^2H_{11/2}$ and $^4S_{3/2}$ levels to the $^4I_{15/2}$ level, respectively. ΔE is the energy gap between the $^2H_{11/2}$ and $^4S_{3/2}$ levels. T is the absolute temperature, and k is the Boltzmann constant. The pre-exponential constant is given by $C = g_H A_H \omega_H / g_S A_S \omega_S$. Fig. 3 shows the schematic of energy level and the upconversion mechanism for the Er^{3+}/Yb^{3+} system under 980 nm excitation.

In order to investigate influence of photo-thermal behavior, the emission spectrum of film and powder as comparison were recorded at various excitation power (Fig. 4), respectively. Under 980 nm excitation, the $Gd_2(MoO_4)_3$:Er^{3+}/Yb^{3+} phosphor emits two green bands centered at 525 and 545 nm which originate