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Research paper

Thermal and pump power effect in $SrMoO_4$:Er^{3+}-Yb^{3+} phosphor for thermometry and optical heating

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ABSTRACT

The pump power and temperature dependence study in the Er^{3+}-Yb^{3+} codoped $SrMoO_4$ phosphors for the green UC emission bands has been investigated by using two NIR (980 nm and 808 nm) laser radiation. The thermometric behaviour of the codoped phosphor operated in the 300–543 K gives maximum sensitivity $\sim 25.5 \times 10^{-3}\ K^{-1}$ for 980 nm excitation whereas, for 808 nm excitation the maximum sensitivity is $\sim 21.5 \times 10^{-3}\ K^{-1}$ over 300–465 K. The optical heating study upon two NIR laser radiations has also been performed. The experimental observations made in this article may be of significant interest for thermometry and optical heating.

1. Introduction

Phosphors are generally prepared by doping the rare earth (RE) ions in the suitable low phonon frequency host materials. The research in the field of REs doped phosphors has been growing due to their various technological applications such as in light emitting diodes (LEDs), display devices, optical temperature sensing, nanoheating and solar cell efficiency enhancement [1–5]. In recent years, frequency upconversion (UC) phenomenon has become an effective way of producing visible light by using near infrared (NIR) diode laser excitation [6–8]. The singly Er^{3+} doped phosphors show lower upconversion efficiency because of low absorption cross-section in the near infrared region. The Yb^{3+} ions having large absorption cross-section corresponding to the $^2F_{7/2} \rightarrow {}^2F_{5/2}$ absorption transition in the NIR region may act as a sensitizer and hence effectively improve the upconversion efficiency [8,9]. The energy transfer mechanism between the RE ions has been considered a better approach for generating the improved UC emission intensity in the Er^{3+}-Yb^{3+} codoped systems [10]. Among the molybdate based materials, the strontium molybdate ($SrMoO_4$) exhibits better host due to its better thermal and chemical stability [11]. $SrMoO_4$ host is a wide band gap ($\sim$3.72 eV) material, in which Mo is coordinated by four O^{2-} atoms in tetrahedral symmetry [11,12].

The optical transitions with small energy separation arising from the REs doped phosphors under near infrared (NIR) laser diode excitation may be suitable for fluorescence intensity ratio (FIR) analysis. The RE doped phosphors not only show the radiative transitions but also they have capability to produce non-radiative transitions followed by the multiphonon emissions. In optical thermometry, intensity ratio of the two closely spaced emission transitions arising from the same rare earth ions or two different rare earth ions at different temperatures are used. Fibre Bragg gratings (FBGs) sensor due to its multiplexing capability, where large number of sensing points can be used along a single optical fibre, are helpful in strain/stress, temperature and vibration detections. However, for optical sensors it is not necessary to make an exchange between photonics and electronics at each sensing point. This may enhance the flexibility of an optical sensor and hence FIR based temperature sensing could be a good choice among other techniques to work as non-contact optical thermometry [13–15]. The trivalent erbium ion is the most important candidates among the other rare earth ions, due to the availability of two closely spaced energy levels ($^2H_{11/2}$ and $^4S_{3/2}$) that could be useful for the study of the optical temperature sensing. The temperature sensing study has been performed in the Er^{3+} doped different hosts viz. Y_2O_3, Gd_2O_3, La_2O_3, $BaMoO_4$, $Yb_2Ti_2O_7$, etc., by using NIR laser diode excitation [8,15–20].

Hyperthermia is a therapeutic technique in which some desired temperature is used to destroy the affected cell, such as tumor and cancer cells. The heating produced by the REs doped phosphor materials could be helpful for hyperthermia treatment. Bednarkiewicz et al. reported that the Nd^{3+} doped $NaYF_4$ colloidal near infrared nanophosphors can be used in photostimulated localized hyperthermia treatment [21]. The NIR radiations based upconverting materials have benefit over the other radiation based materials. The NIR radiations based upconverting materials can minimize the

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tissue autofluorescence losses, increases light penetration depth and favourable for bioimaging [21,22]. Du et al. reported that the Er^{3+}-Yb^{3+} codoped $SrMoO_4$ phosphors prepared by using high temperature solid state reaction method can be used in temperature sensor with low sensitivity $\sim 12.8 \times 10^{-3}\ K^{-1}$ at 480 K [23].

The present article reports, the temperature sensing and optical induced heating in the Er^{3+}-Yb^{3+} codoped $SrMoO_4$ phosphors synthesized through the chemical co-precipitation method under 980 nm and 808 nm laser diode excitations.

2. Experimental

2.1. Materials and phosphor preparation

All the raw materials with 99.9% purity viz. strontium carbonate ($SrCO_3$), ammonium hepta-molybdate tetra hydrate $(NH_4)_6Mo_7O_{24}{\cdot}4H_2O$, erbium oxide ($Er_2O_3$), ytterbium oxide ($Yb_2O_3$) have been taken to synthesize the Er^{3+}/Er^{3+}-Yb^{3+} doped/codoped $SrMoO_4$ phosphors by using chemical co-precipitation method [24]. A series of phosphors were prepared by keeping erbium ions concentration fixed at 0.3 mol% and ytterbium ions concentration was varied from 1.0 to 5.0 mol%. The compositional equation accountable for the preparation of doped/codoped phosphors are given as follows,

$$99.7\ \text{mol\%}\ SrMoO_4 + 0.3\ \text{mol\%}Er_2O_3$$

$$(99.7 - x)SrMoO_4 + 0.3\ \text{mol\%}\ Er_2O_3 + x\ \text{mol\%}Yb_2O_3$$

where x = 1.0–5.0 mol%.

The appropriate amounts of weighted raw materials were dissolved in conc. HNO_3 acid to convert them into their respective nitrates. Then after NH_4OH solution was added into the solution to get precipitate. The precipitate was collected by using filter paper and heated in an electric furnace at $\sim$500 °C to get the as-synthesized phosphors. Finally, the as-synthesized phosphors were annealed at $\sim$800 °C temperature for 3 h. The annealed phosphors were used further for all characterization purposes.

2.2. Measurements and characterization

The crystal structure of the prepared Er^{3+}-Yb^{3+} codoped $SrMoO_4$ phosphors have been analyzed by X-ray powder diffraction (XRD) analysis (Bruker D8 focus diffractometer). The XRD patterns of all the developed phosphors have been recorded by using Cu Kα radiation source (λ = 0.154 nm) [24]. The upconversion (UC) emission spectral performance at different pump power densities has been performed by using continuous wave (CW) 980 nm and 808 nm NIR laser diode sources by using a monochromator (Princeton: Acton SP-2300) attached with the photomultiplier tube (PMT) operated through a personal computer. The temperature dependence UC emission study in the prepared phosphor has been carried out by putting the sample inside a homemade small furnace. The temperature of sample kept into a small furnace controlled by using Varivolt has been monitored via K type thermocouple placed at $\sim$2.0 mm distance apart from the sample.

3. Results and discussion

3.1. Absorption study

Fig. 1 shows the absorption spectrum of the optimized 0.3 mol% Er^{3+}-2.0 mol% Yb^{3+} codoped $SrMoO_4$ phosphor in 400–1000 nm wavelength range. Four absorption bands around $\sim$490 nm, $\sim$520 nm, $\sim$655 nm and $\sim$808 nm assigned by the electronic absorption transition of Er^{3+} ion from the $^4I_{15/2}$ (ground level) to different excited levels viz. $^4F_{7/2}$, $^2H_{11/2}$, $^4I_{15/2}$, $^4F_{9/2}$, and $^4I_{9/2}$ have been observed. Also, one broad absorption band around $\sim$980 nm has been detected in the codoped phosphor due to the combined effect of both the dopants (Er^{3+} and Yb^{3+}) corresponding to the $^4I_{11/2} \leftarrow {}^4I_{15/2}$ and $^2F_{5/2} \leftarrow {}^2F_{7/2}$ absorption transitions.

3.2. Temperature sensing study

UC emission spectra of the codoped phosphors (keeping erbium ions concentration fixed at 0.3 mol% and varying the ytterbium ions concentration up to 5.0 mol%) prepared by co-precipitation method upon excitation at 980 nm have been recorded and 0.3 mol% Er^{3+}-2.0 mol%Yb^{3+} combination was found to be optimum [24]. Fig. 2(a) and (b) shows the UC emission spectra of the optimized 0.3 mol% Er^{3+}-2.0 mol% Yb^{3+} codoped $SrMoO_4$ phosphor upon 980 nm and 808 nm laser diode excitations at $\sim$34.87 W/cm^2 and $\sim$40.12 W/cm^2 pump power density in 510–560 nm wavelength range. The UC emission bands observed in the green region has been assigned through the $^2H_{11/2} \rightarrow {}^4I_{15/2}$ and $^4S_{3/2} \rightarrow {}^4I_{15/2}$ transitions. The two-photon absorption process is found to be responsible for the generation of the upconversion emission bands lying in the green region under NIR diode laser excitation [24,25–27]. The origination of the UC emission bands and their dynamic energy migration mechanisms have been explained elsewhere [24].

In order to show the applicability of the Er^{3+}-Yb^{3+} codoped $SrMoO_4$ phosphor in the optical thermometry, the fluorescence intensity ratio (FIR) analysis for the $^2H_{11/2} \rightarrow {}^4I_{15/2}$ and $^4S_{3/2} \rightarrow {}^4I_{15/2}$ transitions of the Er^{3+} ion by using 980 nm and 808 nm laser diode sources at different temperatures has been performed. The UC emission spectra upon excitations at 980 nm and 808 nm diode laser at $\sim$34.87 W/cm^2 and $\sim$40.12 W/cm^2 at two different temperatures are shown in Fig. 2(a) and (b). The band positions of both the green UC emission bands arising from the codoped phosphor do not change with the variation of temperature. The FIR varies from 1.82 to 7.53, when the temperature is raised from 300 K to 543 K under 980 nm laser diode excitation at $\sim$34.87 W/cm^2 (Fig. 2(a)) whereas, the variation in FIR is from 1.60 to 4.83 when the temperature is raised from 300 K to 465 K under 808 nm laser diode excitation at $\sim$40.12 W/cm^2 (Fig. 2(b)). On further increasing the temperature, the UC emission peaks do not appear clear and becomes noisy due to the thermal quenching effect and hence it becomes difficult to measure the FIR due to the low signal to noise ratio [28,29]. The FIR of two thermally coupled energy levels only depends on energy level separation (energy gap) and temperature of the sample [13,18,30,31]. The variation of FIR with temperature upon excitation with the 980 nm (34.87 W/cm^2) and 808 nm (40.12 W/cm^2) laser diode excitations is shown in Fig. 3(a). From Fig. 3(a), it is clear that the FIR values are similar upon two NIR laser diodes excitations operating at 980 and 808 nm. The small mismatch in the FIR values (error = ±7%) is due to the difference in the pump power (34.87 W/cm^2 for 980 nm and 40.12 W/cm^2 for 808 nm) density for the two laser diodes and fluctuations in the current/voltage during different scans. From this, it is concluded that the FIR for a sample at the same temperature is independent of the pump wavelengths.

The FIR for both the green UC emission bands corresponding to the $^2H_{11/2} \rightarrow {}^4I_{15/2}$ and $^4S_{3/2} \rightarrow {}^4I_{15/2}$ transitions respectively at temperature 'T' can be represented as [13,18,32],

$$\mathbf{FIR} = \frac{\boldsymbol{I_{H\rightarrow I}}}{\boldsymbol{I_{S\rightarrow I}}} = \mathbf{A}\ \exp\left(-\frac{\boldsymbol{\Delta E}}{\boldsymbol{kT}}\right) \tag{1}$$

where $I_{H\rightarrow I}$ and $I_{S\rightarrow I}$ are the integrated intensities of green emission bands for the $^2H_{11/2} \rightarrow {}^4I_{15/2}$ and $^4S_{3/2} \rightarrow {}^4I_{15/2}$ transitions respectively. 'A' is a constant, 'ΔE' is the energy gap between the $^2H_{11/2}$