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$(Y_{0.968}Er_{0.002}Yb_{0.030})_2O_3$ Upconverting Particles as Optical Heater

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Abstract

The optical heating of upconverting particles and its surrounding volume has a vital role in biomedical and therapeutic applications. The internal self-heating in $(Y_{0.968}\,Er_{0.002}\,Yb_{0.030})_2O_3$ upconverting particles synthesized by urea assisted combustion route has been detected under 980 nm diode laser excitation. A temperature rise up to 348 K has been computed using fluorescence intensity ratio (FIR) method of the thermalized upconversion emission bands due to $^2H_{11/2}\rightarrow{}^4I_{15/2}$ and $^4S_{3/2}\rightarrow{}^4I_{15/2}$ transitions of Er^{3+}ion. The results indicate that the material is an interesting candidate for optical heater in biomedical applications.

Keywords: Upconversion, Optical heating, Fluorescence intensity ratio (FIR), Photoluminescence, Phosphors, Biomedical applications, Thermographic phosphors, Temperature sensors, Optical thermometry, Nanoheater, Temperature, Measurement, Applications, Laser, Fluorescence, Luminescence, Nonradiative relaxation, Thermal population, Optical material, Rare earth, Erbium, Thermal probe, Heating effect, Combustion, Laser diagnostics, Yttrium oxide, Optical sensors, Laser material

Introduction

The upconversion (UC) emission based materials have been a subject of interest because of their utility in extensive field of applications such as biological imaging, biological sensor, photodynamic therapy, temperature sensors, display devices, security printing, solar cell, etc. [1–5]. Among these applications, optical temperature sensors are one of the most demanded applications. Optical temperature sensors are considered to be attractive alternatives to the conventional temperature sensors due to their ability to sense temperature remotely where physical access is not possible. The temperature sensing performance of some rare earth doped upconverting materials have been studied recently [6–8]. The temperature dependent fluorescence intensity ratio (FIR) of two closely lying energy levels (thermally coupled) of a rare earth ion is studied at different temperatures [7–11]. The technique also includes the variation of FIR of the Stark sublevels in single rare earth ion and two closely lying levels of different rare earth ions [12,13]. As the laser light irradiates the material, some heat is generated due to laser excitation. The laser induced heating in the upconverting materials has been reported rarely [14–17]. The internal heating in Yb^{3+}/Er^{3+} doped fluoride nanoparticles up to 1073 K has been detected by Tikhomirov et al. [14],whereas Singh et al. [15] have investigated the laser induced optical heating in Er^{3+}/Yb^{3+}codoped Gd_2O_3phosphor by monitoring the $^2H_{11/2}\rightarrow{}^4I_{15/2}$and $^4S_{3/2}\rightarrow{}^4I_{15/2}$transitions of Er^{3+}ions. Hayakawa et al. [16] have observed the optical heating in the Er^{3+} doped TeO_2-ZnO-Nb_2O_5 glass. Suo et al. [17] have also studied the laser induced optical heating in Tm^{3+}/Yb^{3+}codoped $Ba_5Gd_8Zn_4O_{21}$ up-conversion (UC) phosphors using stark levels ($^1G_{4(1)}$, $^1G_{4(2)}$) of $Tm^{3+}$and observed rising of sample temperature from 278.8 to 321.8 K with increasing pump power from 638 to 1802 mW. Laser induced heating was also studied using Ho^{3+}/Yb^{3+} ions in $Ca_{12}Al_{14}O_{33}$ phosphor by monitoring the green emissions coming from the Ho^{3+}ion [18].

In this work we prepared $(Y_{0.968}\,Er_{0.002}\,Yb_{0.030})_2O_3$ particles by solution combustion route and the laser induced heating in $(Y_{0.968}\,Er_{0.002}\,Yb_{0.030})_2O_3$ upconverting particles by monitoring the intensity ratio of two green emission bands of Er^{3+} ions upon near infrared (NIR) excitation is reported. The self-heating of the particles have been calculated employing temperature dependent FIR study of the synthesized material and based on the observed results the utilization of the material for probable applications is concluded herein.

Experimental

The $(Y_{0.968}\,Er_{0.002}\,Yb_{0.030})_2O_3$ particles have been synthesized through urea assisted combustion process [19]. This process has advantages over other usual techniques, e.g. low synthesis temperature, uniform mixing, high purity, less energy consumption, etc. Since, nitrate forms of the precursors are used in combustion synthesis; the staring materials namely, the Er_2O_3, Yb_2O_3 and Y_2O_3 were dissolved in concentrated nitric acid to prepare their nitrates. The optimized composition for the upconversion emission of the sample was taken according to the given formula

96.8mol% Y_2O_3+0.2mol% Er^{3+}+3.0mol% Yb^{3+}

The nitrates were mixed with urea solution and the whole mixture was stirred for 3 h at 343 K on a magnetic stirrer with 800 rpm rotation speed. Due to this vigorous stirring, the material became a transparent gel. This gel was then transferred to an alumina crucible and placed inside a preheated furnace at 773 K. Combustion with auto-ignition takes place and a fluffy white mass is produced. The as-obtained powder is further annealed at 1123 K for 2 h and used for further characterization purposes.

TheX-ray diffraction(XRD) were recorded over the angular range 10°≤ 2θ≤ 80° using Cu-kα(1.5405 Å) radiation by a Bruker D8 Advance X-ray diffractometer with a scanning rate of 4 degree per minute. A continuous wave NIR diode laser of 980 nm wavelength was used as excitation source for the sample. The sample was kept inside a homemade heat chamber. The laser beam was 0.70 mm in radius and was focused on the sample by adjusting the collimating optics. A thermocouple was placed at very close (~2 mm) to the focal spot of laser on the sample. The temperature dependent and pump power dependent upconversion spectra recorded. The laser beam was set at 10 $Wcm^{-2}$and the spectra were recorded at different temperatures. For temperature dependent measurements the laser was chopped with an optical chopper.

Results and discussion

The X-ray diffraction pattern of the annealed sample is shown in Figure 1 and the pattern was matched well with JCPDS card no. 25-1200 that shows cubic phase structure with lattice constant 10.60 Å. The main peaks observed at 20.77°, 29.47°, 34.09°, 48.79°, 57.76°, and 79.15° correspond to the (211), (222), (400), (440), (622), and (662) planes, respectively.

The upconversion emission spectra of the sample have been recorded in 500–600 nm range upon 980 nm diode laser excitation and are shown in Figure 2a. The green emission bands are observed at ~524 nm and ~550 nm corresponding to the $^2H_{11/2}\rightarrow{}^4I_{15/2}$ and $^4S_{3/2}\rightarrow{}^4I_{15/2}$ transitions of Er^{3+}ion respectively.

It is seen from the figure that on increasing excitation power the emission intensity of two bands are not varying equally

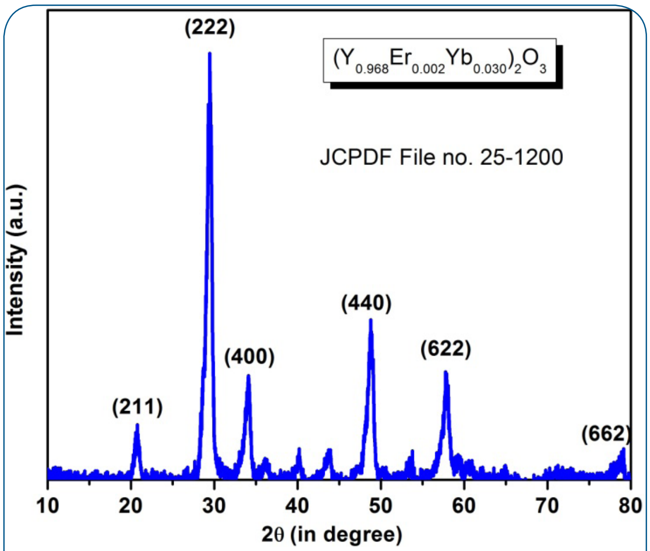

Figure 1: X-ray diffraction pattern of $(Y_{0.968}\ Er_{0.002}\ Yb_{0.030})_2O_3$ particles

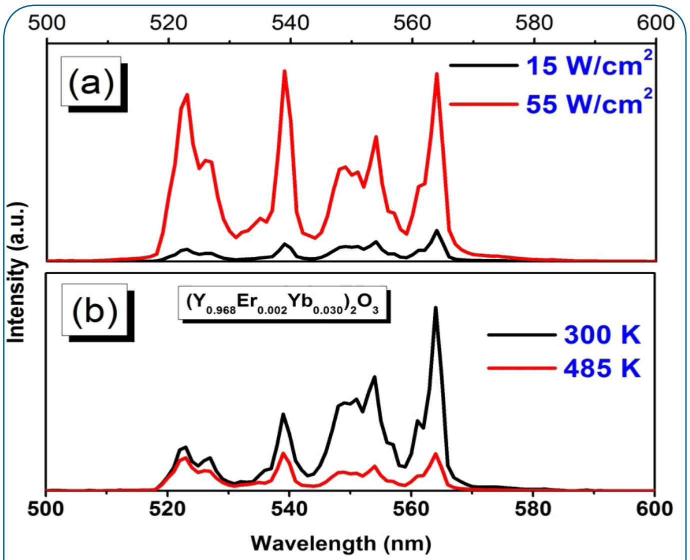

Figure 2: Upconversion emission spectra (a) pump power dependent (b) temperature dependent

rather the ratio of the two emission bands (I_{524}/I_{550}) varies in a systematic way with excitation power. It is well known that the variation in ratio of emission intensity of two close lying levels of rare earth (RE) ions is because of the change in populations in the corresponding levels[10,18,20]. The energy separation between $^2H_{11/2}$ and $^4S_{3/2}$ levels is ~770 cm^{-1} and the variation in population of these two levels obey Boltzmann's distribution law [11]. So, the observed variation in intensity ratio is due to change in population and this observation gives rise the concept of laser induced optical heating. For experimental verification of the idea of optical heating, the fluorescence intensity ratio as a function of laser pump power has been calculated and is shown in Figure 3a. The variation of upconversion emission spectra at different excitation powers are shown in Figure 2b. It is observed that the

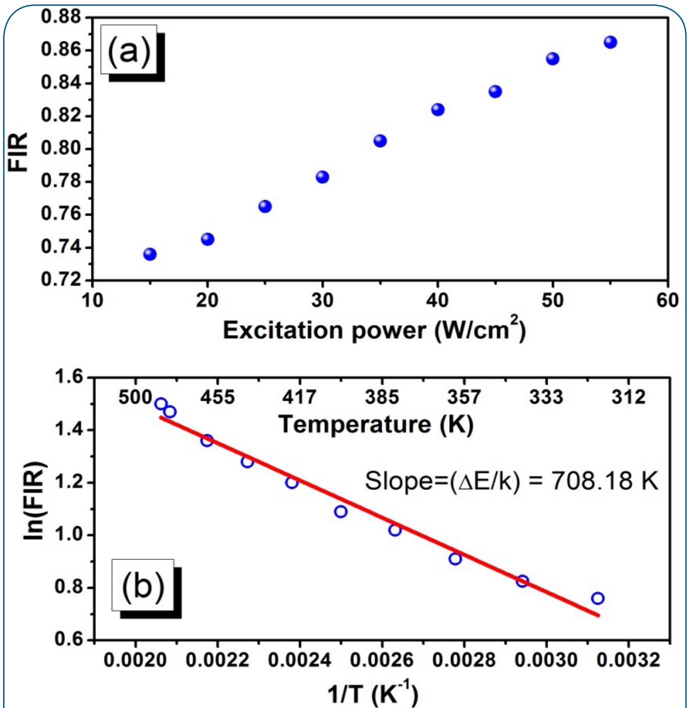

Figure 3: (a) Plot of fluorescence intensity ratio as a function of input pump power density (b) The monolog plot of the FIR (I_{524}/I_{550}) as a function of inverse absolute temperature

position of the emission bands do not change with temperature, only the intensities of the bands change. This change in intensity is due to change populations of $^2H_{11/2}$and $^4S_{3/2}$levels. The integrated fluorescence intensity ratio of transitions $^2H_{11/2}\rightarrow{}^4I_{15/2}$and $^4S_{3/2}\rightarrow{}^4I_{15/2}$could be represented according to Wade et al. [10]:

$$FIR=\frac{I_{524}(^2H_{11/2}\rightarrow{}^4S_{15/2})}{I_{550}(^4S_{3/2}\rightarrow{}^4I_{15/2})}=\frac{W_H g_H h\upsilon_H}{W_S g_S h\upsilon_S}\exp(-\frac{\Delta E}{k_B T})=B\exp(-\frac{\Delta E}{k_B T})\quad(1)$$

where, I_{524} and $I_{550}$are the integrated intensities corresponding to $^2H_{11/2}\rightarrow{}^4I_{15/2}$ (~524 nm) and $^4S_{3/2}\rightarrow{}^4I_{15/2}$ (~550 nm) transitions of Er^{3+}, WH and WS are the radiative probabilities of the two transitions, g_H and g_S are the degeneracies of $^2H_{11/2}$ and $^4S_{3/2}$ levels, respectively, and $h\nu_H$ and $h\nu_S$ are the photon energies of the $^2H_{11/2}\rightarrow{}^4I_{15/2}$ and $^4S_{3/2}\rightarrow{}^4I_{15/2}$ transitions respectively, ΔE is the energy gap between the two emitting levels, k_B is the Boltzmann constant and T is absolute temperature. The above equation can be expressed as follows:

$$\ln(FIR)=\ln(B)+(-\frac{\Delta E}{k_B T})\quad(2)$$

where, B is a constants. The energy separation, ΔE changes very little with host materials. The value of B depends on the response of the detection system, degeneracy of the emitting levels and spontaneous emission probabilities.

A plot of ln(FIR) vs. 1/T is shown in Figure 3b. The experimental data can be fitted linearly according to equation (2). The slope of the fitting represents ΔE/k value. The energy difference according to the fitting is calculated as 492 cm^{-1}(Boltzmann's constant, k=0.695 $cm^{-1}K^{-1}$) and lnB= 2.90.

The calculated values of FIR in pump power dependent and temperature dependent measurements are co-related. In both the cases the variation of FIR is due to the variation of temperature. Therefore, the laser induced heating have been calculated using the experimental values of ΔE/k and lnB. The temperature gain of the material due to laser irradiation is depicted in Figure 4. It is seen that as the pump power increases, the temperature of the material also increases. The temperature of the materials is found to increase from 320 K to 348 K as the pump density increases from 15 W/cm^2 to 55 W/cm^2. The generation of heat in the material is due to the involvement of non-radiative relaxations. The probability of multiphonon transition (W) at temperature T between the two energy levels can be expressed as [21]:

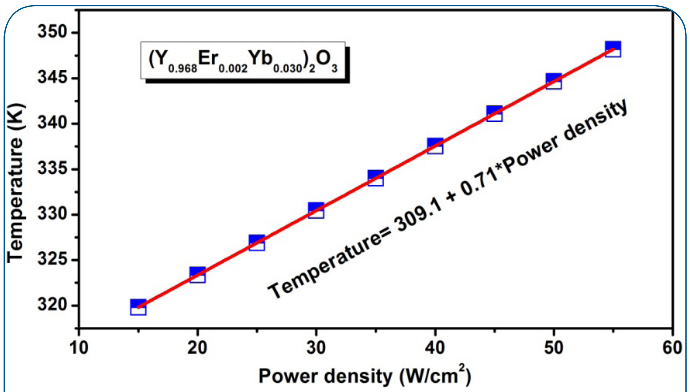

Figure 4: Temperature gain in $(Y_{0.968}Er_{0.002}Yb_{0.030})_2O_3$ particles as a function of pump density.

$$W_{nr}(T)=W_{nr}(0)\left(1-e^{-h\nu/kT}\right)^{-n}\quad(3)$$

where, 'n' is the number of phonons involved in bridging the energy gap, hν is the phonon energy and 'k' is the Boltzmann constant. At a fixed value of n, the non-radiative decay rates, $W_{nr}(T)$ increases exponentially with temperature.It is also to be noted that at low temperature, higher nonradiative rates can be achieved at lower value of 'n'. The strong electron-phonon coupling in nanocrystalline particles also enhances nonradiative transitions [14-17]. Therefore, the generation of heat in the present material may be due to stronger electron-phonon coupling and involvement of lower number of phonons in multiphonon relaxation. The results suggest that the laser induced heat generation in the $(Y_{0.968}Er_{0.002}Yb_{0.030})_2O_3$ particles could be useful for hyperthermia based treatment [14,15].

Conclusions

The laser induced heating in $(Y_{0.968}Er_{0.002}Yb_{0.030})_2O_3$ upconverting particles has been detected successfully upon NIR laser excitation. The cubic phase structured $(Y_{0.968}Er_{0.002}Yb_{0.030})_2O_3$ particles were synthesized by urea assisted solution combustion route. The pump power dependent upconversion emission and temperature dependent upconversion emission were correlated to measure the laser induced heating of the material. Though the generated heat in the material is not too high, still the temperature gain in this material is in the physiological range.So, the present material may be useful in biomedical applications (viz. hyperthermia treatment).

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