



THERMO LUMINESCENT PROPERTIES AND AFTERGLOW STUDY OF THE RARE EARTH DOPED Y_2O_3 NANOPHOSPHORS

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ABSTRACT

In this work, green emitting $Y_2O_3:Tb^{3+}$ nanophosphors were synthesized by the combustion method. These prepared materials were characterized by using scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction techniques (XRD) and fourier transform infrared spectroscopy (FTIR). XRD studies confirmed the body centered cubic structure of Tb doped Y_2O_3 nanophosphors. Thermoluminescence of $Y_2O_3:Tb^{3+}$ nanophosphors have been investigated. TL emission spectra show intense peak around 545 nm. PL decay characteristics of the Tb doped Y_2O_3 nanoparticles in the form of powder were measured.

Keywords: Nanophosphors, Y_2O_3 , Combustion Method, Thermoluminescence

I. INTRODUCTION

Lanthanides or the Rare Earths have found increasing use in the past 100 years. There are many applications of the lanthanides like : use in display phosphors for TVs and computer monitors, as phosphors in fluorescent lights, as probes to determine the structure of biomolecules, as dopants in fiber optic cable decrease losses, as strengtheners in metals, in materials for solid state lasers, and as luminescent materials for many products.

In lanthanides, the energies of the $4f \rightarrow n$ transitions correspond mostly to the visible region of the electromagnetic spectrum, resulting in their use for optical applications. In most cases, the emission from the rare earth ions is due to optical transitions within the $4f \rightarrow n$ configuration (e.g. Tb^{3+} ($4f_8$)). The $4f$ orbital lies inside the ion and therefore it is well shielded from the surroundings by the filled $5s_2$ and $5p_6$ orbitals so that the $4f$ electrons are less influenced by the environment of the lanthanide ion [1,2]

A number of studies have been reported on the luminescent properties of $Y_2O_3:RE$ (Rare earth) nanoparticles and luminescence was found to depend strongly on the nature of the synthesis method and condition employed.[3-7] We have also studied the Thermoluminescence (TL) and Mechanoluminescence (ML) of Eu doped Y_2O_3 nanophosphor [8] , and Photoluminescence (PL) and Electroluminescence(EL) of the Eu,Tb codoped of the Y_2O_3 [9]. In this paper, we obtain the Y_2O_3 : Eu nanocrystalline phosphors by combustion method. The present paper deals with the Thermoluminescent properties as well as the photoluminescent decay of Tb doped Y_2O_3 were measured. To the best of our knowledge, no study has reported PL decay characteristics of the Tb doped Y_2O_3 nanoparticles in the form of powder.

II. EXPERIMENTAL TECHNIQUE

2.1 Preparation Technique

Tb-doped Y_2O_3 nanophosphors were prepared by the combustion synthesis method using Terbium oxide (Tb_2O_3) (99.99%, Sigma Aldrich), yttrium oxide (Y_2O_3) (99.99%, Sigma Aldrich), nitric acid (HNO_3) and urea ($CO(NH_2)_2$) as the starting raw materials. Tb-doped samples were prepared by mixing $Y(NO_3)_3$ and $Tb(NO_3)_3$ according to the formula $(Y_{1-x}Tb_x)_2O_3$ ($x = 0.01-0.07$). A suitable amount of urea was added to the mixture of the corresponding nitrate solution keeping urea to metal nitrate molar ratio as 2.5. The corresponding mixture was then dissolved properly to achieve a uniform solution. Finally this sample was transferred to crucible and heated by introduced into muffle furnace at $600^\circ C$. The synthesis reaction was as follows



2.2 Characterization of the Sample

A number of experimental techniques are employed to yield structural information of prepared samples. In present investigations, all the sample were characterized by Transmission electron microscopy (TEM) and X-ray techniques (XRD), Scanning electron microscopy (SEM). X-ray diffraction of the prepared phosphors was recorded in a wide range of Bragg angle 2θ using a Bruker D8 advanced X-ray diffraction (XRD) measuring instrument with Cu target radiation ($\lambda = 0.154\ 056\ nm$). The Fourier transform infrared (FTIR) spectra were recorded in the wavenumber range $4000-400\ cm^{-1}$ using a Shimadzu FTIR spectrometer. TEM of the prepared phosphors were done by using Philips CM10 microscope. SEM of the prepared phosphors were done by using Zeiss EVO40 microscope. For recording TL, samples were exposed to UV radiations at different time. TL glow curves were recorded with the help of TLD reader (Model 1009I). The afterglow intensity and decay curves were obtained at room temperature using a brightness meter. Before decay curves measurement, each sample was exposed to standard UV lamp for 10 minutes.

III. RESULTS AND DISCUSSION

3.1 Structural Characterization

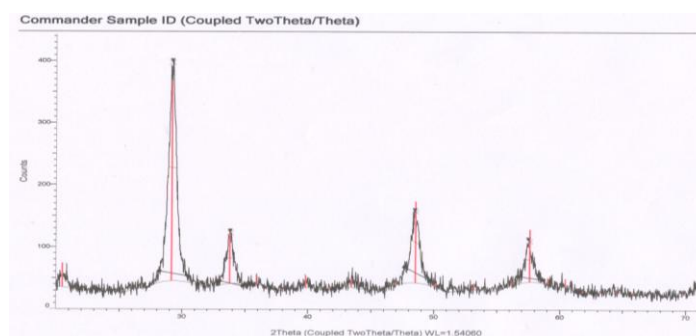


Fig 1. XRD OF Y_2O_3 : Tb (3 mole %)

Fig (1) shows the XRD pattern of the Y_2O_3 : Tb (3 mole %). The XRD pattern of all the sample indicate 4 diffraction peaks of cubic structure at $2\theta = 29.12^\circ$, 33.78° , 48.50° and 57.63° corresponding to (2 2 2), (4 0 0), (4 4 0) and (6 2 2). The peak positions of the entire specimen showed (2 2 2) peak with highest intensity in the XRD patterns. All the XRD peaks could be indexed to the cubic phase of Y_2O_3 (JCPDS No. 411105) with space group Ia3 (206). The crystalline size has been estimated from the broadening of the first diffraction peak using

Debye-Scherrer formula $R = K\lambda / \beta \cos\theta$, Where R is crystallite size ,K is constant , θ is Bragg angle, λ is wavelength and β is Fullwidth at half maxima(FWHM) of the peak .The average particle size of the $Y_2O_3:Tb$ sample has been obtain 55.2 nm.

Table 1:Structural parameter of the $Y_2O_3:Tb$ phosphor

Sample	Peaks	$2\theta(\text{deg})$	$\cos\theta$	FWHM	h,k,l	$d(\text{nm})$	$a(\text{\AA})$	Volume	Particle size(nm)
$Y_2O_3:Tb$ (3mole %)	I peak	29.16	0.9677	0.59	-2,-2,-2	3.06	10.58	1184.8	55.2
	II peak	33.79		0.46	-4,0,0	2.65			
	III peak	48.54		0.54	-4,-4,0	1.87			
	IV Peak	57.63		0.71	-6,-2,-2	1.60			

3.2 Fourier Transform Infrared Spectroscopy (FTIR)

The FTIR spectra fig (2) consist mainly three parts: the first part, with a broad peak at around 3440 cm^{-1} , due to O-H vibration; the second part ,showing peaks at 1518 cm^{-1} , 1405 cm^{-1} and 842 cm^{-1} , due to C-O asymmetric stretching and deformation, due to absorption of CO_2 ;and the third part at 572 cm^{-1} , assigned to the absorption of Y_2O_3 . Overtone or combination band located in the range $2000\text{--}1667\text{ cm}^{-1}$.

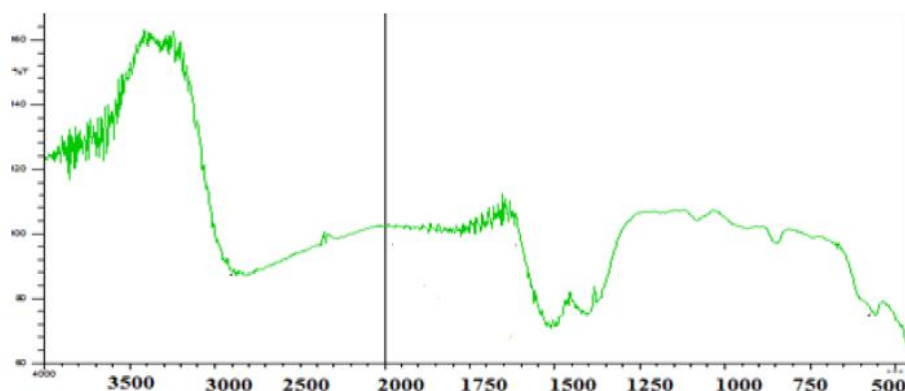


Fig 2 FTIR spectra of $Y_2O_3:Tb$ (3 mole %)

3.3 Scanning Electron Microscopy (SEM)

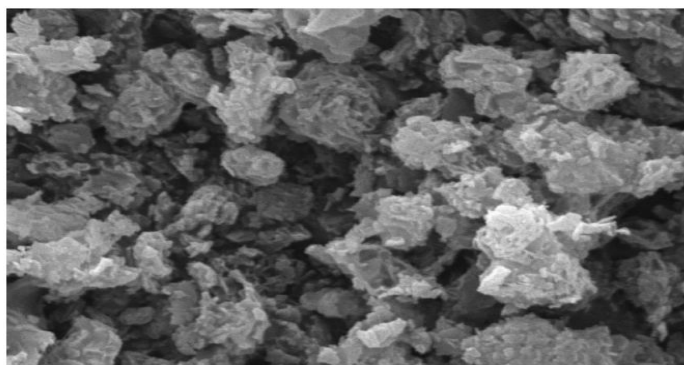


Fig 3 SEM picture of $Y_2O_3:Tb$ (3 mole%) nanophosphor

Fig (3) represents the SEM image of the Y_2O_3 : Tb (3 mole %) nanophosphor. For Y_2O_3 : Tb (3 mole %) made by combustion method a spongy-like structure is clearly seen. The SEM observations show that the size distribution was broad and particles are agglomerated and form a continuous network. Particles are porous and irregular that is often the case for powders derived from metal nitrates .

3.4 Transmission Electron Microscopy (TEM)

A perfect spherical morphology with a mean size of 100 nm is found for Fig (4) Tb doped Y_2O_3 . The aggregated particle sizes are found to be in the range of 100-150 nm. The particle size obtained from the TEM image is larger than that obtained from XRD linewidths and this has been attributed to the fact that linewidths depend on the presence of coherent domains in the sample, whereas the TEM technique does not have that requirement and measures the actual particle size.

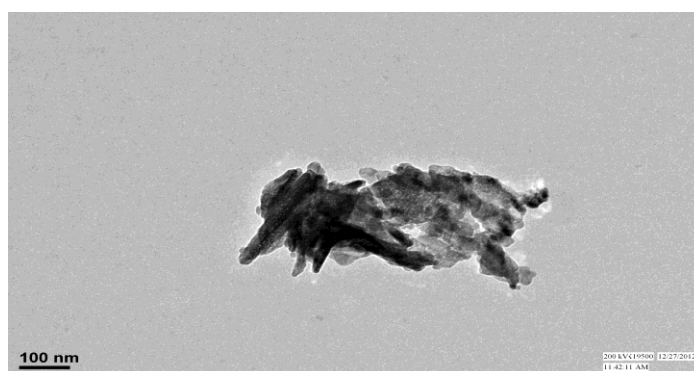


Fig 4 TEM image of Tb doped Y_2O_3 (3 mole%)

3.5 Photoluminescence Decay (PL decay)

The afterglow intensity and decay curves were obtained at room temperature for Y_2O_3 : Tb phosphor shown in fig (5). The afterglow intensity and decay curves were obtained at room temperature using a brightness meter (Konica Minolta LS-100). Before decay curves measurement, each sample was exposed to standard UV lamp for 10 minutes.

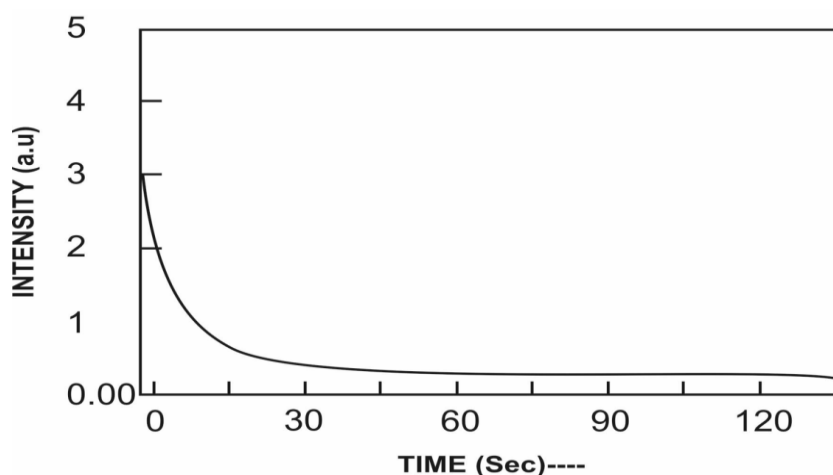


Fig.5: PL decay curve of Tb doped Y_2O_3 (3 mole%)

We can observe that the decay kinetics of Sample $\text{Y}_2\text{O}_3:\text{Tb}$ is faster, which relates to the trap depth of the material – probably the traps are located deeper in the forbidden zone for Sample $\text{Y}_2\text{O}_3:\text{Tb}$. We can observe a long tail the intensity 3 minutes after the termination of irradiation which descends very slowly.

Calculation of decay constant for $\text{Y}_2\text{O}_3:\text{Tb}$

The decay constant was calculated using the following formula

$$\text{Decay constant (T)} = t_2 - t_1 / 2.303 (\text{Log } I_1 - \text{Log } I_2)$$

(1) Fast decay constant = .60 ms

(2) Slow decay constant = 6.42 sec

3.6 Thermo luminescence

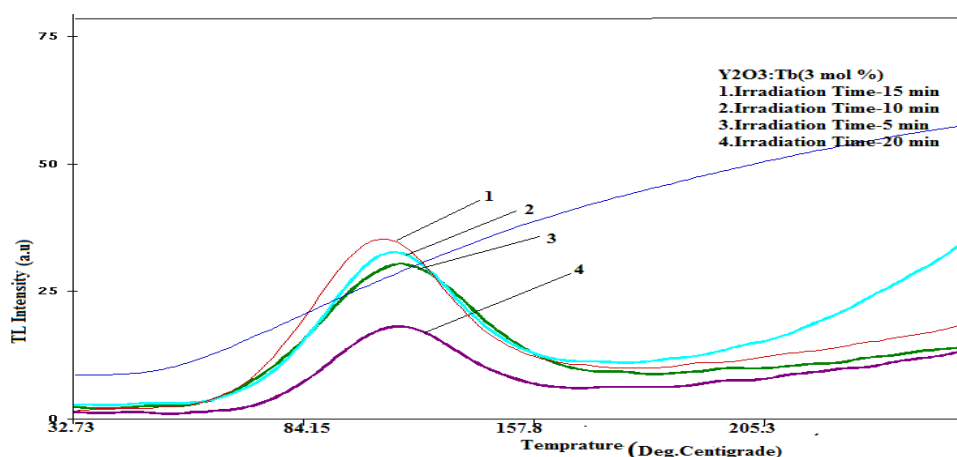


Fig.6 shows the TL glow curve of UV-irradiated $\text{Y}_2\text{O}_3:\text{Tb}$ nanophosphor for different irradiation time. The TL glow curve show single peak at 102°C . It is seen that the TL intensity increases with increasing irradiation time and attains maximum at 15 min UV irradiation time and then decreases with further increase in irradiation time. The terbium-doped yttria phosphor presents a TL glow curve with one peaks (T_{max}) centered around 102°C .

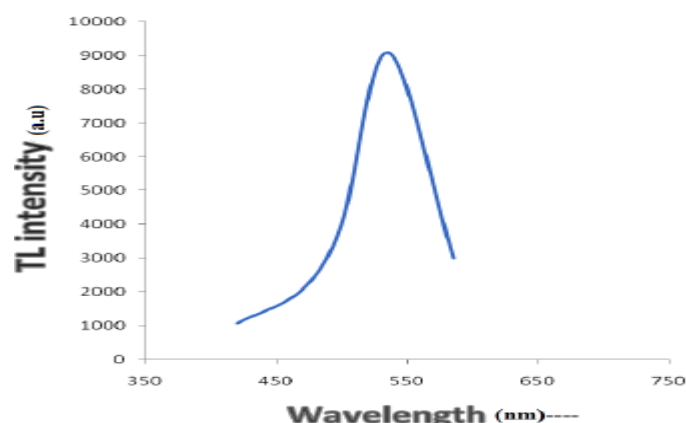


Fig 7 TL emission spectra of $\text{Y}_2\text{O}_3:\text{Tb}$

Figure 7 shows the TL spectrum of $\text{Y}_2\text{O}_3:\text{Tb}$ ranges from 300 to 700 nm. The strongest emission band occurs at 520 nm due to the $^5\text{D}_4 \rightarrow ^7\text{F}_5$ characteristic transition of green emission for Tb^{3+} .

Thermoluminescence is a good way to detect the recombination emission caused by detrapping of carriers thermally. The energy corresponding to the glow peak is equal to the trap depth. What we must point out is that traps and carriers (electrons and holes) may be produce by irradiation, but they are also able to be created during

sample processing.

RE^{3+} ion acts as a recombination center affecting the TL response of the Y_2O_3 material. As the particles become smaller, ions at the surface increase rapidly. In nanoparticles, most ions at the surface are not saturated in coordination; Electrons or holes may be excited easily and escape from the ions and they are trapped at surface states located in the forbidden gap. When the sample is heated the electrons are detrapped and their subsequent recombination with holes gives rise to the light emission. The TL intensity is increased for higher exposed time because the concentration of traps are increased by increasing exposure time of UV radiation. The trapping centers provide energy states available between valance band and conduction band responsible for radiative recombination.

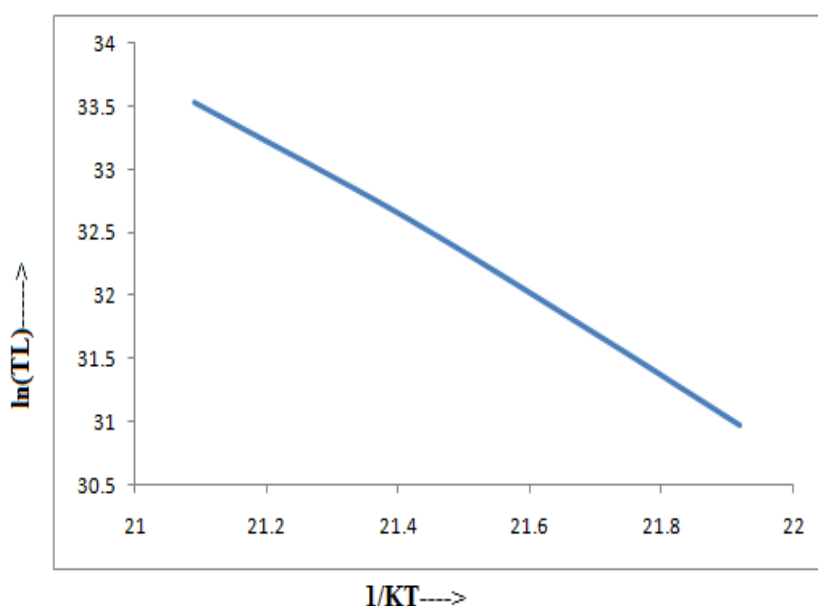


Fig 8 IR method for second peak of $\text{Y}_2\text{O}_3\text{:Tb}$ (3mole% concentration)

S.No	Sample name (mole%)	For Ist peak	For 2 nd peak
2.	$\text{Y}_2\text{O}_3\text{:Tb}$ (3mole%)	0.67	

Table 2: The TL parameters of RE doped Y_2O_3 by Initial rise method

The shape of the TL glow curve is strongly influenced by the order of the kinetics. In half width method the temperature T_m , T_1 and T_2 which are respectively, the peak temperature and temperature on lower(T_1) and upper(T_2) sides corresponding to half the peak intensity shown in fig 3.4 and dependent on the shape of the glow curve, are utilized to form equation to relate E to all or some of these temperatures. Using only the ascending part of a glow peak, one finds the value of E for the first order kinetics.

$$E = 1.51(T_m T_1)/(T_m - T_1)$$

Where as the descending part of a glow peak is used, the value of E is expressed as $E = k T_m^2/(T_2 - T_m)$

S.No	Sample name(mole%)	For Ist peak
2.	Y ₂ O ₃ :Tb (3 mole%)	0.69 eV

Table 3: The TL parameters of RE doped Y₂O₃ by Half- Width method

The order of kinetics and the activation energy of glow curve was found using Chen's empirical formulae. Theoretically the form factor μ_g is found using formula

$$\mu_g = (T_2 - T_m) / (T_2 - T_1).$$

Where, T_m is the peak temperature at the maximum and T_1 and T_2 are respectively, the temperatures on either side of T_m , corresponding to half intensity. The trap depth or the thermal energy needed to free the trapped electrons can be calculated using the following equation

$$E_a = c_a (kT_m)^{2/\alpha} - b_a (2kT_m)$$

$$\alpha = \tau, \delta, \omega,$$

$\tau = T_m - T_1$ is the half width at the low temperature side of the peak

$\delta = T_2 - T_m$ is the half width toward the fall-off side of the glow peak

$\omega = T_2 - T_1$ is the total half-width

$\mu = \delta / \omega$ is so called geometrical shape or symmetry factor

$$c_\tau = 1.51 + 3.0 (\mu_g - 0.42), \quad c_\delta = 0.976 + 7.3 (\mu_g - 0.42)$$

$$c_\omega = 2.52 + 10.2 (\mu_g - 0.42),$$

$$b_\tau = 1.58 + 4.2(\mu_g - 0.42), \quad b_\delta = 0, \quad b_\omega = 1$$

Using the value of T_m , T_1 and T_2 from the experimentally obtained maximum TL glow curve in Fig.4 the form factor of Y₂O₃:Tb (3 mole%) is found 0.54, which shows first order kinetics in it.

Sample	Maximum peak temperature (T_m)	Order of kinetics(b)	Activation energy (E)			
			E_δ	E_ω	E_τ	E_{avg}
Y ₂ O ₃ : Tb (3 mole %)	383	1 st order	.66	.68	.70	.68

Table 4: The TL parameters of Tb doped Y₂O₃ by Chen's empirical method

IV. CONCLUSIONS

The preparation of RE doped Y₂O₃ nanophosphors for different concentration of doping material using a combustion method appears to be more feasible for production. Decay constant of Y₂O₃: Tb³⁺ (3 mole%) is (i) fast decay is .60 ms and (ii) slow decay constant is 6.42sec. From PL decay curve, We can observe that the decay kinetics of Sample Y₂O₃:Tb is faster, which relates to the trap depth of the material – probably the traps are located deeper in the forbidden zone for Sample Y₂O₃:Tb. We can observe a long tail the intensity 3 minutes after the termination of irradiation which descends very slowly. The TL properties of Y₂O₃: Tb nanophosphor



has been investigated for UV irradiation and the trapping parameters were calculated. The phosphor Y_2O_3 is found to have first order kinetics in TL emission suggesting recombination of charge carriers.

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