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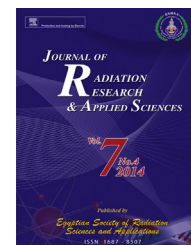


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# Gamma ray induced thermoluminescence studies of yttrium (III) oxide nanopowders doped with gadolinium

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## ABSTRACT

Y<sub>2</sub>O<sub>3</sub>:Gd<sup>3+</sup> nanophosphor was prepared by the solid state reaction method. Systematic studies have been done to investigate the structural and optical properties of the gadolinium doped Y<sub>2</sub>O<sub>3</sub> phosphor. The prepared phosphor was characterized by using X-ray diffractometer (XRD), scanning electron microscopy (SEM), transmission electron microscopy and UV–VIS–NIR spectrophotometer. The XRD patterns reveal that these prepared phosphors have cubic phase crystal structure. SEM and TEM images showed uniform doping of the material over the entire materials. The energy band gap for gadolinium doped Y<sub>2</sub>O<sub>3</sub> phosphor was revealed from the optical studies and was found to 5.1 eV. The prepared phosphors were also examined by thermoluminescence technique. The kinetic parameters like trap depth, frequency factor were calculated by using the Peak shape method, which are discussed in details. The TL Glow curves were fitted in CGCD (computerized glow curve convolution deconvolution) technique & trapping parameters calculated. The TL parameters such as activation energy for deconvoluted peak were found in the range of 0.82–2.24 eV. The frequency factor is of the order of between of  $1.78 \times 10^{12}$  and  $9.84 \times 10^{20} \text{ s}^{-1}$ .

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## 1. Introduction

Trivalent rare earth ion doped oxide host materials have widely studies due to its potential application in the field of biotechnology and materials science. Oxide based host materials having low phonon energy, higher thermal-chemical

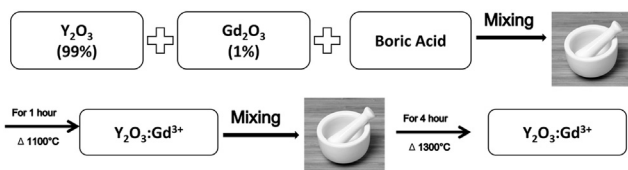
stability and higher luminescence efficiency. Due to the low phonon energy the non radiative transition is less (Bisen, Sharm, Brahme, & Tamrakar, 2009; Chen, Liu, Liang, Somesfalean, & Zhang, 2008; Tamrakar, 2012; Tamrakar & Bisen, 2013a, 2013b; Tamrakar, Bisen, & Brahme, 2014; Tamrakar, Bisen, Robinson, Sahu, & Brahme, 2014a, 2014b). Currently the size of this oxide materials are reduced in the

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**Scheme 1 – Synthesis of  $Gd^{3+}$  doped  $Y_2O_3$  phosphor.**

nanorange, have attracted several researches from different fields such as in the field of luminescence. It has been found that the several properties of individual nano particles can be different from those of their bulk. Recent studies on different luminescent nano materials have showed that they have potential application in optical response (Tamrakar, 2012; Tamrakar, 2013; Tamrakar et al., 2013, 2014b).

Yttrium (III) oxide ( $Y_2O_3$ ) has considerable attentions in literature due to its intriguing physical properties likes as most stable compounds and used in high performance luminescence devices, magnet, catalysts and other functional materials because of their optical, chemical and electronic characteristics (Matsuura, 2002; Tamrakar et al., 2013; Zhou, Lin, & Wang, 2003).  $Y_2O_3$  has a sesquioxide type material and is a well-known host matrix for RE ions containing intriguing physical properties. The  $Y_2O_3$  host matrix presents a higher melting point (2380 °C), higher thermal conductivity, a wide transparency range, high refractive index ( $\approx 1.8$ ) and low cut off phonon energy (380  $cm^{-1}$ ), all making it a very promising host material for the production of efficient luminescent media (Tamrakar et al., 2013; Dubey et al., 2014).  $Y_2O_3$  is considered as an attractive host material for  $Gd^{3+}$  because  $Gd_2O_3$  and  $Y_2O_3$  have similar crystal structures and  $Gd^{3+}$  and  $Y^{3+}$  ions have nearly the same ionic radii (Matsuura, 2002; Tamrakar, 2012; ; Vetrone, Boyer, & Capobianco, 2003).

Different synthetic routes have been reported in literatures for the preparation of oxide nanophosphor such as sol–gel,

solid state reaction, hydrothermal, combustion, co-precipitation etc (Matsuura, 2002; Nalwa, 2000; Tamrakar et al., 2013; Vetrone, Boyer, & Capobianco, 2004). The high temperature solid-state reaction method has produced desirable phosphors. So it is useful due to the advantage of high purity, easy to prepare, low cost and good homogeneity etc (Tamrakar et al., 2013, 2014b).

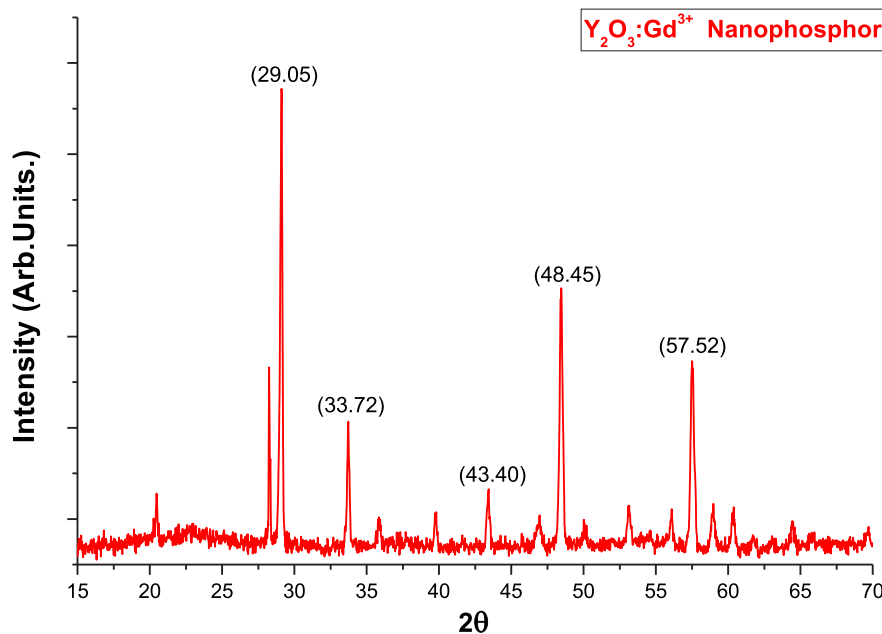
In the present study, we have prepared gadolinium doped  $Y_2O_3$  nanophosphor by a high temperature solid state reaction method using boric acid as a fuel. The prepared sample was characterized for their structural and optical properties.

## 2. Solid state synthesis of $Y_2O_3:Gd^{3+}$ phosphor

$Y_2O_3:Gd^{3+}$  phosphor was synthesized by conventional solid state method. Oxide of rare earth materials such as yttrium oxide ( $Y_2O_3$ ), gadolinium oxide ( $Gd_2O_3$ ) and boric acid as a flux with high purity (99.99%) were used as precursor materials to prepare  $Gd^{3+}$  doped  $Y_2O_3$  phosphor. In stoichiometric ratios of rare earth ions  $Gd^{3+}$  (1 mol%) and  $Y_2O_3$  were used to synthesize  $Y_2O_3:Gd^{3+}$  phosphor. These chemicals were weighed and grinded into a fine powder by using agate mortar and pestle. The grinded sample was placed in an alumina crucible and heated at 1100 °C for 1 h followed by dry grinding and further heated at 1300 °C for 4 h in a muffle furnace. The sample is allowed to cool at room temperature in the same furnace for about 15 h (Tamrakar et al., 2014, 2014a, 2014b) (Scheme 1).

### 2.1. Characterization of prepared phosphor

Crystalline phases and sizes of as-prepared phosphors were characterized by powder X-ray diffraction (XRD; Bruker D8 Advance). The morphology and particle sizes of  $Y_2O_3:Gd^{3+}$  phosphor were observed by transmission electron microscopy



**Fig. 1 – Powder XRD pattern of  $Y_2O_3:Gd^{3+}$  (1%) doped phosphor.**

**Table 1 – Values of  $2\theta$  with corresponding value of FWHM  $b$ , crystallite size ( $D$ ), micro-strain ( $\epsilon$ ), and dislocation density of solid state reaction synthesized cubic of  $Y_2O_3:Gd^{3+}$  (1%) doped phosphor.**

$2\theta$ (in radian)	FWHM (radian)	Particle size (nm)	Strain ( $\text{line}^{-2} \text{m}^{-4}$ )	Dislocation density ( $\times 10^{15} \text{line/m}^2$ )
29.05	0.15	52.97	0.2343743914	0.356424017
33.72	0.15	52.97	0.2205875886	0.356423659
43.40	0.18	44.14	0.2499991784	0.513249522
48.45	0.21	37.83	0.2763147776	0.698588841
57.52	0.24	33.11	0.2608681654	0.912437903

(Philips CM-200), and FE-SEM (JSM-7600F). The optical absorption spectra of the films were obtained by using Chemito, double beam UV–VIS–NIR spectrophotometer (SPEC-TRASCAN-UV-2600). All of the measurements were performed at room temperature.

### 3. Results and discussion

#### 3.1. XRD analysis results

Fig. 1 shows the XRD pattern of  $Gd^{3+}$  doped  $Y_2O_3$  phosphor. The average particle size was calculated by Debye–Scherrer formula (Guinier, 1963)

$$D = \frac{k\lambda}{\beta \cos \theta}$$

Here,  $k = 0.89$  constant,  $d$  is the crystallite size for the  $(hkl)$  plane,  $\lambda$  is the wavelength of the incident X-ray radiation [ $CuK\alpha$  (0.154 nm)],  $\beta$  is the full width at half maximum (FWHM) in

radians, and  $\theta$  is the diffraction angle for the  $(hkl)$  plane. From the PXRD pattern, it was found that the prominent phase formed is  $Y_2O_3$ , after the diffraction peaks as well indexed based on the ICDD no. 89-5591. This reveals that the structure of  $Y_2O_3$  is cubic. The average crystallite size was found to be 43.6 nm.

The strain ( $\epsilon$ ) developed in the prepared phosphor can be calculated from the relation (Birkholz, 2006; Wilson, 1949)

$$\epsilon = \frac{\beta_{2\theta} \cot \theta}{4}$$

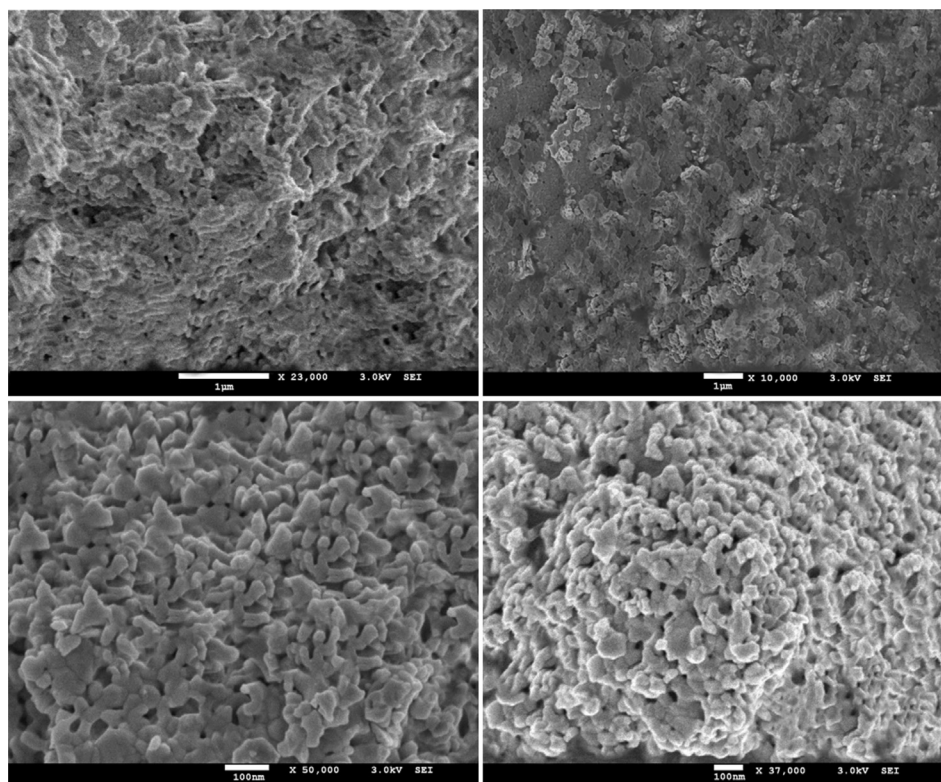
where  $\theta$  and  $\beta_{2\theta}$  have their usual significances. In general, the crystallite size is inversely proportional to the micro-strain. The strain values of the prepared  $Y_2O_3:Gd^{3+}$  phosphor are given in Table 1. A dislocation is a linear defect in a crystal. The dislocation density, defined as the length of dislocation lines per unit volume of the crystal. Unlike vacancies and interstitial atoms, dislocations are not equilibrium imperfections, i.e. thermodynamic considerations are insufficient to account for their existence in the observed densities. It can be calculated by Williamson and Smallman's relation (Birkholz, 2006; Wilson, 1949; Wagner & Aqua, 1965)

$$\delta = \frac{n}{D^2}$$

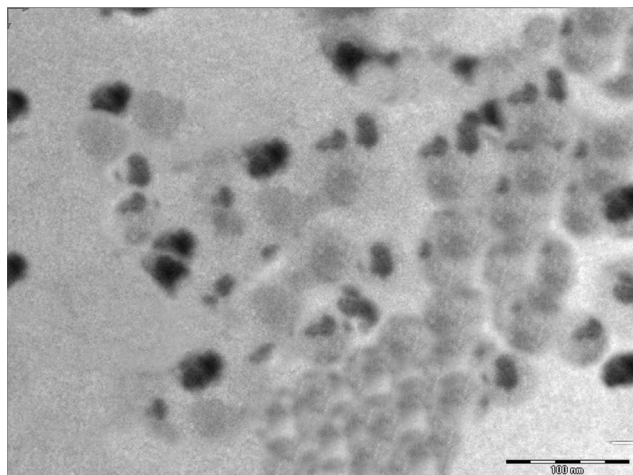
where  $n$  is a factor, which equals unity giving minimum dislocation density and  $D$  is the crystallite size. The minimum values of dislocation density is found to be  $\approx 0.356 \times 10^{15} \text{line/m}^2$ .

#### 3.2. Scanning electron microscope (SEM)

Fig. 2 shows the morphology of  $Y_2O_3:Gd^{3+}$  (1%) doped phosphor by SEM technique with different resolution. The



**Fig. 2 – SEM images of prepared  $Y_2O_3:Gd^{3+}$  (1%) phosphor.**



**Fig. 3 – Transmission electron microscopy (TEM) image of  $Y_2O_3:Gd^{3+}$ .**

synthesized sample shows good morphology and connectivity with grains and formation of nano sized prepared sample. We have seen that by the SEM micrograph the particle size distribution is uniform over the entire surface of the  $Y_2O_3:Gd^{3+}$ .

### 3.3. Transmission electron microscopy (TEM)

Transmission electron microscopy image is shown in Fig. 3. The image confirm the formation of nanophosphor. The prepared sample shows a compact distribution over the surface and good connectivity between grains. Similarly in HRTEM image particle size is in good agreement with XRD pattern.

### 3.4. Optical studies

The optical absorption and Tauc relation graph of  $Y_2O_3:Gd^{3+}$  are displayed in Fig. 4[A] and [B] respectively. These spectra were recorded in the wavelength range 200–500 nm at room temperature in air. During scanning process, quartz cuvettes with pure solvent is placed in one of the beam direction used as reference another quartz cuvettes, in which solution of

$0.2\text{ g } Y_2O_3:Gd^{3+}$  was taken, in the other beam's direction. The absorption spectra of the prepared phosphor was presented in Fig. 4[A] and [B]. The optical absorption spectra depend on the chemical composition, crystal structure, energy of incident photon, film thickness, and films surface morphology. The important observation drawn from the study of spectra is that the fundamental edge shifted towards longer wavelengths, when doping is happened in phosphor.

The optical data were analyzed by the following classical relation (Tauc relation) (Tamrakar, 2012; Tamrakar & Bisen, 2013a)

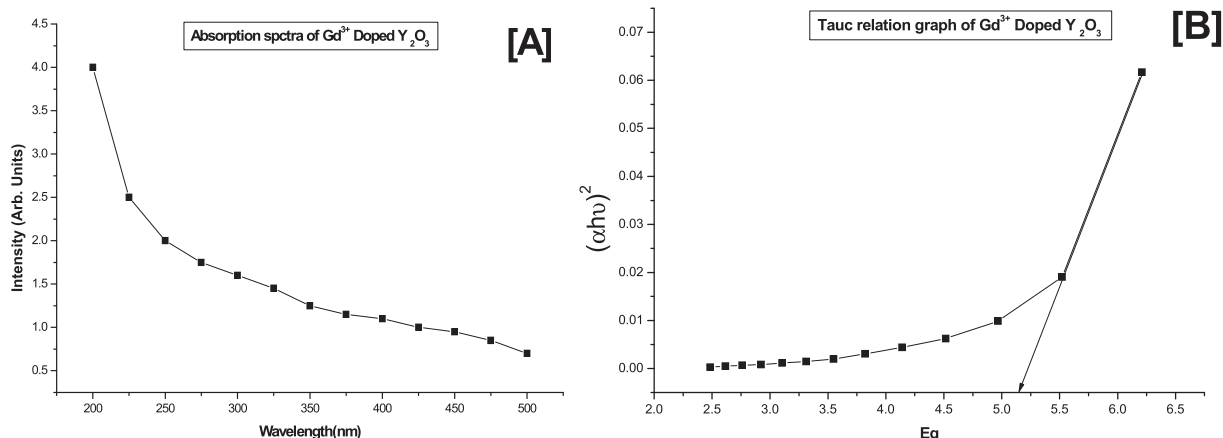
$$(\alpha h\nu)^2 = A(h\nu - E_g)^{n/2}$$

where  $h\nu$  is the photon energy,  $E_g$  is the band gap energy,  $A$  and  $n$  are constant.  $A$  is related to the effective masses associated with the valence and conduction bands. For allowed direct transitions, the value of  $n$  is equal to 1 and for forbidden direct transition  $n$  is equal to 3. For indirect allowed transitions  $n$  is equal to 4 and for indirect forbidden transition  $n$  is equal to 6. The energy band gap of the films is calculated by plotting  $(\alpha h\nu)^2$  versus  $E_g$ . A plot of  $(\alpha h\nu)^2$  against  $E_g$  axis yields the optical band gap. The absorption edge is found at 243 nm. The band gap was calculated corresponding to absorption edge (243 nm). The band gap was found to be 5.15 eV for  $Y_2O_3:Gd^{3+}$  phosphors (Tamrakar, 2012; Tamrakar & Bisen, 2013a).

### 3.5. Thermoluminescence studies of $Y_2O_3:Gd^{3+}$ phosphors for gamma ray

Prepared phosphor was examined by thermoluminescence technique under gamma rays. Fig. 5 shows the thermoluminescence studies of  $Y_2O_3:Gd^{3+}$  phosphors for 2 kGy gamma ray. We found a broad peak at 244° C (Lochab et al., 2007; Mckeever, 1986) (Fig. 6).

$Y_2O_3:Gd^{3+}$  nanopowder material was done using glow curve deconvolution (CGCD) functions suggested by Kitis, Gomez-Ros, and Tuyn (1998) for first, second and general order glow curves, respectively. The TL glow of  $Y_2O_3:Gd^{3+}$  phosphor could be deconvoluted in to three glow peaks, with peaks at 222, 255 and 299 K. The estimated kinetic parameters for  $Gd^{3+}$  doped  $Y_2O_3$  phosphor were calculated by curve fitting techniques CGCD curve of experimental data. The overlapping glow peaks



**Fig. 4 – Absorption spectra [A] and Tauc-relation graph [B] of  $Y_2O_3:Gd^{3+}$  phosphors.**

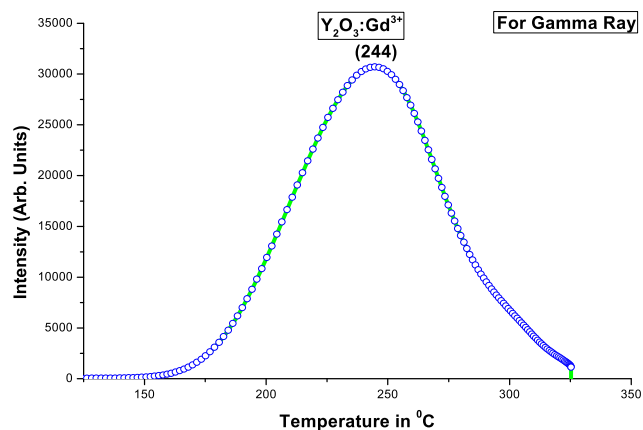


Fig. 5 – TL Glow curve for  $Y_2O_3:Gd^{3+}$  for 2 kGy gamma ray.

(main peak) can lead to the broadening of the glow peak and consequently appear to lower the value of trap depth and higher the value of frequency factor (Puchalska & Bilski, 2006). Trap parameters were calculated using Chen's method (Chen, 1969; Chen & Kirsh, 1981; Chen, Lawless, & Pagonis, 2011; Chen & Mceever, 1997; Chen & Pagonis, 2011; Vij, 1993). The glow peaks were deconvoluted using the software "peak fit" calculated TL parameters are tabulated in Table 2. The estimated kinetic parameters for prepared phosphor are calculated by curve fitting techniques CGCD curve of experimental data and the peak shape method proposed by Chen and others (Chen, 1969; Chen & Kirsh, 1981; Tamrakar et al., 2014, 2014a, 2014b). The activation energy is found in between 1.08 and 2.33 eV and the frequency factor is range of  $1.78 \times 10^{12}$  to  $9.84 \times 10^{20}$  for gamma irradiated phosphor (Bisen, Robinson, Sahu, & Brahme, 2014b).

#### 4. Conclusion

$Y_2O_3:Gd^{3+}$  doped phosphor was successfully synthesized by the solid state reaction method by using boric acid as a flux. XRD pattern confirms that synthesized sample shows cubic

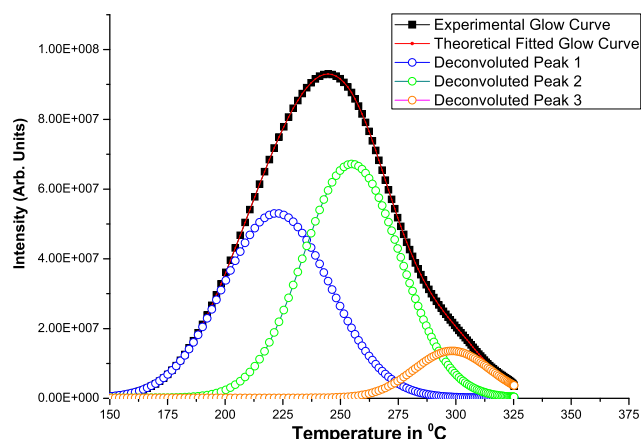


Fig. 6 – Deconvoluted glow curve for  $Y_2O_3:Gd^{3+}$  for 2 kGy gamma ray.

Table 2 – Trapping parameters of a typical glow curve. There are no any appreciable changes in the peak temperatures of the deconvoluted peaks and the trapping parameters with the impurity concentration.

Peaks	$T_1$ (°C)	$T_m$ (°C)	$T_2$ (°C)	$\mu_g$	$b$	$E$ (eV)	$S$ ( $s^{-1}$ )
Peak 1	193	222	248	0.47	1.49	1.08	$1.78 \times 10^{12}$
Peak 2	228	255	281	0.49	1.52	1.33	$9.06 \times 10^{13}$
Peak 3	280	299	316	0.47	1.49	2.33	$9.84 \times 10^{20}$

structure. The average crystallite size was found to be 43.6 nm. XRD studies confirm the phosphor is in single phase and is in nanorange. SEM and TEM results were confirmed the XRD results. The absorption edge is found at 243 nm and corresponding band gap calculated, was found to be 5.15 eV for  $Y_2O_3:Gd^{3+}$  phosphors. In thermoluminescence, peaks were fitted by CGCD technique the curves in symbols are the theoretically fitted curves and a very good fit could be seen between the experimental and theoretical curves for  $Gd^{3+}$  doped  $Y_2O_3$  phosphor. The impurity doped in the material could help in generating more number of electron traps and hole traps/luminescent centers, which is responsible for TL. The TL parameters such as activation energy for deconvoluted peak were found in the range of 1.08–2.33 eV. The frequency factor is of the order of between of  $1.78 \times 10^{12}$  and  $9.84 \times 10^{20} s^{-1}$ .

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