

Thermoluminescence and Kinetic Parameters of γ-Exposed Sr₃B₂O₆:Sm³⁺ Nanophosphors

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Abstract— In this paper, we have studied the thermoluminescence (TL) response of Sm^{3+} doped $\text{Sr}_3B_2O_6$ nanophosphors synthesized by combustion method using metal nitrate as precursor and urea as fuel. A broad TL peak was observed at 400K with a shoulder at 500K. The crystalline structure of the nanophosphors was confirmed by X-ray powder diffraction with the average crystallite size of 41 nm which was cross verified by transmission electron microscopy. The samples were irradiated with a γ -dose using ⁶⁰Co source in the range 1000 Gy – 5000 Gy at room temperature. The effect of different heating rates at a fixed dose has also been discussed. TLAnal program and Chen's method were used to determine the kinetic parameters such as activation energy (E), order of kinetics (b), and frequency factor (s) of different peaks present in the $\text{Sr}_3B_2O_6:\text{Sm}^{3+}$ nanophosphor.

Keywords— Combustion synthesis; X-ray diffraction; Thermoluminescence.

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1. INTRODUCTION

Thermoluminescence requires the perturbation of a system by an ionizing radiation from a state of thermodynamic equilibrium, via the absorption of external energy, into a metastable state, which is followed by a thermally stimulated relaxation of the system back to its equilibrium condition. In thermal equilibrium condition, i.e. T = OK, all the defect levels, up to the Fermi level F, are occupied by electrons. The other levels are empty electrons and crystal lattices are in thermal equilibrium. Under irradiation the electrons in the defect levels or in the valence band gain energy and rise into higher levels, beyond the Fermi level. After the irradiation distribution process takes place and the excited system goes back to equilibrium. The time required for going back to equilibrium may vary from milliseconds to years, depending on the material, its defects and the temperature [1]. The polycrystalline TL materials exhibit a glow-curve having one or more maxima, called glow-peaks, each corresponding to an energy level trap formed by thermal stimulation.

This glow curve is a graphical representation of the luminescence intensity as a function of heating time or temperature, providing information about parameters corresponding to each peak, such as activation energy, frequency factor(s) and the order of the kinetics. TL depends on the material, the type of impurity, radiation induced defect centers, dose and type of ionizing radiation strongly [2,3].

Moreover, borates are considered to be the most important host materials, many authors have prepared and studied TSL glow curves and TSL emission characteristics using thermoluminescent (TL) technique [4,5]. Alkaline earth borates have very low cost, easy handling, long duration phosphorescence characteristics and high quantum efficiency therefore its wide applications in field of luminescence have been explored [6]. Strontium borate belongs to the rhombohedral structure with a space group of R-3c.

To the best of our knowledge, the thermoluminescence properties for $Sr_3B_2O_6:Sm^{3+}$ by high-dose γ irradiation have not yet been reported in the literature. In the present work, the thermoluminescence (TL) properties of $Sr_3B_2O_6:Sm^{3+}$ were determined by TLAnal program and Chen's method. Also, kinetic parameters such as activation energy (E), order of kinetics (b), and frequency factor (s) of different peaks present in the $Sr_3B_2O_6:Sm^{3+}$ nanophosphor was studied.

1.1 Experimental

High purity chemicals $Sr(NO_3)_2$, H_3BO_3 , NH_2CONH_2 , Sm_2O_3 and HNO_3 purchased from HIMEDIA were used as starting materials. The samples were synthesized with different molar concentration of Sm^{3+} dopant. Starting materials were taken in a stoichiometric composition, such that the metal nitrates oxidizer to fuel ratio becomes unity. The mixture of starting materials was grinded with the help of agate mortar pastel using few drops of ethanol

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for about 30-40 minutes in order to get a homogeneous mixture. This paste is then kept in furnace preheated to about 600°C which leads to rapid dehydration and foaming, followed by yellow flame resulting into white porous foamy product within 3 minutes. After combustion the foamy product was cooled at room temperature. Then the samples were grinded to get a fine powder annealed at 900 ⁰C for 3hrs. To confirm the phase the samples were characterized by X-ray Diffractometer by Bruker Advance D8 X-ray diffractometer with Cu K α radiation (= 0.15406nm). For TL spectroscopy, the samples were pre-exposed to γ -radiation at room temperature by using a gamma chamber containing a ⁶⁰Co source at the Health Physics Laboratory at Inter University Accelerator Centre, New Delhi. The TL glow curves of the exposed phosphors were recorded by taking 5 mg of the sample each time on the HARSHAW QS 3500 TLD reader, at different heating rate 3K/s, 5K/s and 10K/s.

1.2 Results and Discussion

1.2.1 X-Ray Diffraction Study

The pattern exhibits the existence of a pure phase $Sr_3B_2O_6$ which matches well with JCPDS card No-31-1343 as in fig. 1. $Sr_3B_2O_6:Sm^{3+}$ samples after annealing show rhombohedral structure with a space group of R-3c and lattice constants a = 9.0552 Å, b= 9.0552 Å, c = 1.2566 Å, cell volume = 8.9603 Å³ and were calculated using Unitcellwin software [7]. The average crystallite size was calculated by using Scherrer's equation [8] from the most intense peaks.

$$d = \frac{0.89\lambda}{\beta \cos \theta R}$$

Where d is the average crystallite particle size, λ is the incident wavelength of CuK α (1.54 Å) radiation, β is the full-width at half maximum (in radians) and θ_B is the Bragg angle. The average particle size of the prepared phosphor was found to be 41nm.



Fig. 1: XRD patterns of JCPDS Card No 31-1343 and Sr₃B₂O₆:Sm³⁺ nanocrystalline phosphor.

1.2.2 Thermoluminescence Study

The effect of different dose of γ -radiations (1000Gy - 5000Gy) on the TL glow curve of Sr₃B₂O₆:Sm³⁺ nanophosphor was investigated. Fig. 2 shows the TL peak intensities of Sr₃B₂O₆:Sm³⁺ nanophosphors as a function of γ -ray dose. The figure shows a glow curve having a glow peak at 400^oC with its shoulder at 500^oC. It can be observed that the peak intensity increases with the increase in dose. This is due to the fact that as dose increases number of luminescent center increases which leads to increase in peak intensity i.e. higher the exposure to ionizing radiation, higher number of electrons and holes are trapped hence the TL intensity peak increase with an increasing γ -ray dose [9].



Fig. 2: TL Glow curve of $Sr_3B_2O_6:Sm^{3+}$ nanocrystalline phosphor after different γ -radiation doses.

A graph is plotted between TL intensity and absorbed dose as shown in fig. 3 and our experimental data is found to have linear fit with 0.98066 as R^2 value. This linear relationship is possible when the TL signal from phosphor (Q_{TL}) is proportional to dose (D) and yield or efficiency (Y_{TL}) of thermoluminescent emission is constant [10].



Fig. 3: Linear dose response curve for Sr₃B₂O₆:Sm³⁺ nanocrystalline phosphor.

The effect of different heating rates on the glow curves has been shown in fig. 4 for $Sr_3B_2O_6$:Sm³⁺ nanocrystalline

phosphor irradiated by γ -ray at 5000Gy. From the TL glow curves at heating rates 3K s⁻¹, 5 K s⁻¹ and 10 K s⁻¹ for a dose of 5000 Gy it has been observed that at peak about 400° C, as the heating rate is increased from 3 K s⁻¹ to 5 K s⁻¹ the peak intensity increases and then on further increasing the heating rate i.e. from 5 K s⁻¹ to 10 K s⁻¹ the peak intensity decreases. Also, instead of main peak intensity at 400°C for 10 K s⁻¹ two peaks can be noticed one of them has its peak intensity below 400°C and the other has its peak intensity above 400°C. Fig. 5 clearly shows these two peaks in the main peak after deconvolution by TLAnal program. That means on increasing the heating rate, peak intensity of these two peaks decreases. This increase in peak intensity with increase in heating rate can be explained by the fact that at lower heating rates the charge carriers which are responsible for producing the desired luminescence have adequate time to get retrapped at the recombination center and are not involve in producing luminescence, whereas when the heating rate is further increased, the phenomena such as thermal quenching of TL intensity due to higher heating rates arises [11,12]. It can be noted that the peak intensity of the shoulder peak which is at about 500°C still increases, unlike the main peak when the heating rate is increased from 5 K s⁻¹ to 10 K s⁻¹ which shows no thermal quenching of TL intensity in the shoulder peak.

1.2.2.1 Kinetic Parameters

TL properties of a phosphor are appreciably influenced by trapping parameters i.e. order of kinetics, trap-depth and the frequency factor. To understand the TL phenomenon in the phosphor, knowledge of the parameter is quiet important.



Fig. 4: TL glow curve for Sr₃B₂O₆: Sm³⁺ nanocrystalline phosphor at 5000 Gy at 3K/s⁻¹, 5K/s⁻¹ and 10K/s⁻¹.

There are many approaches to experimentally determine these parameters. We have used Chen formulism to calculate, kinetic parameters like order of kinetics (b), activation energy (E) and frequency factor (s) for each of the deconvoluted peak of the prepared phosphors exposed at room temperature with γ -radiation (1000 Gy – 5000 Gy).



Fig. 5: TL curve fitting of Sr₃B₂O₆: Sm³⁺ nanocrystalline phosphor irradiated to 5000 Gy.

We have used TL glow curve analyzer program version 1.0.3 for glow curve deconvolution and calculated TLAnal parameters. Fig.4 shows, deconvoluted peaks of $Sr_3B_2O_6:Sm^{3+}$ nanocrystalline phosphor at 5000 Gy with a heating rate of 10K/s analyzed by graphical user interface of TLAnal program. The kinetic parameters of each of the deconvoluted glow peaks of the TL materials were also calculated by Chen's [13-15] set of empirical formulae for the Glow curve method. We have utilized T_m as peak temperature and T_1 and T_2 the low and high temperature at half heights. Theoretically, the value of geometrical factor (μ_g) , gives the order of kinetics, which can be evaluated from equation (1). The values of μ_g for first order kinetics must be close to 0.42 and for second order kinetics μ_g value must be close to 0.52. Also, according to Chen's formulism we have:

$$\mu_g = \frac{T_2 - T_m}{T_2 - T_1} \tag{1}$$

The activation energy (E_{α}) can be calculated from the thermal peak temperature by using the following equation:

$$E_{\alpha} = C_{\alpha} \left(\frac{kT_{m}^{2}}{\alpha} \right) - b_{\alpha} \left(2kT_{m} \right)$$
⁽²⁾

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

 $\tau = T_m - T_1; \delta = T_2 - T_m; \omega = T_2 - T_1$
 $C_{\tau} = 1.51 + 3.0(\mu_g - 0.42);$
 $C_{\delta} = 0.976 + 7.3(\mu_g - 0.42);$
 $C_{\omega} = 2.52 + 10.2(\mu_g - 0.42);$
 $b_{\tau} = 1.58 + 4.2(\mu_g - 0.42);$
 $b_{\delta} = 0; b_{\omega} = 1.$

After calculating activation energy (E) and order of

kinetic (b), the frequency factor (s) was calculated by using following equation :

$$\frac{\beta E}{kT_m^2} = s \exp\left\{\frac{-E}{kT_m}\right\} \left[1 + (Z-1)\Delta_m\right]$$
(3)

For first order

$$I(T) = I_m \exp\left[1 + \frac{E}{kT} \frac{T - T_m}{T_m} - \frac{T^2}{T_m^2} (1 - \Delta) \exp\left\{\frac{E}{kT} \frac{T - T_m}{T_m}\right\} - \Delta_m\right]$$
(4)

For second order

$$I(T) = 4I_m \exp\left\{\frac{E}{kT} \frac{T - T_m}{T_m}\right\} \left[\frac{T^2}{T_m^2} (1 - \Delta) \exp\left\{\frac{E}{kT} \frac{T - T_m}{T_m}\right\} + 1 + \Delta_m\right]^{-2}$$
(5)

Where, I(T) = TL intensity at any temperature T(K).

 I_m = Maximum peak intensity.

E= Activation energy (eV) and $\Delta = 2kT/E$.

Table 1: Activation energy of the deconvoluted peaks of $Sr_3B_2O_6$: Sm^{3+} at 5000 Gy at different heating rate by Chen's method and TLAnal program.

Dose	Peak	T _m (K)	μ _σ	Activation energy(eV)	
			18	Chen's	TLAnal
				method	method
5000 Gy	1	392	0.52	1.09	1.07
-	2	402	0.51	1.31	1.39
	3	490	0.69	1.95	1.99
	4	545	0.51	2.02	2.13
4000 Gy	1	388	0.54	1.27	1.21
-	2	401	0.52	1.45	1.42
	3	487	0.71	1.92	1.99
	4	544	0.52	1.99	2.53
3000 Gy	1	398	0.47	1.23	1.25
	2	412	0.49	1.40	1.47
	3	498	0.69	1.72	1.76
	4	552	0.52	1.86	1.83
2000 Gy	1	398	0.49	1.04	1.11
	2	409	0.52	1.52	1.51
	3	500	0.69	1.86	1.85
	4	550	0.52	2.02	2.05
1000 Gy	1	398	0.49	1.10	1.22
	2	409	0.52	1.51	1.48
	3	502	0.69	1.68	1.68
	4	548	0.50	1.74	1.73

We have reported trapping parameters like activation energy (E), order of kinetics (b) and frequency factor (s) obtained after deconvolution of TL glow peaks of

 $Sr_3B_2O_6$: Sm^{3+} nanocrystalline phosphor at different heating rates by TLAnal and Chen's method in table 1 and table 2 respectively.

Also, the activation energy and frequency factor calculated from both TLAnal program and Chen's method are found to be in good agreement with each other. It can be observed from the table 1 that peak1, peak 2 and peak 4 corresponds to second order kinetics whereas peak 3 corresponds to general order kinetics. The trap levels found from Chen's method are found to vary between 1.04 and 2.02eV with frequency factor ranging from 4.99×10^{13} to $6.53 \times 10^{19} \text{s}^{-1}$. A very high value of frequency factor is due to simultaneous occurrence of localized and delocalized transitions leading to a phenomenon called cascade detrapping [16].

Table 2: Frequency factor of the deconvoluted peaks ofSr₃B₂O₆: Sm³⁺ at 5000 Gy at different heating rate byChen's method and TLAnal program.

Dere		T	Frequency Factor	
Dose	Peak	I_m	Chen's	TLAnal
(0)		(11)	method	method
5000 Gy	1	392	4.99×10^{13}	2.65×10^{13}
	2	402	1.46×10^{16}	11.7×10^{16}
	3	490	6.53×10^{19}	10.8×10^{19}
	4	545	1.87×10^{18}	20.9×10^{18}
4000 Gy	1	388	1.65×10^{16}	2.07×10^{16}
	2	401	87.7×10^{16}	3.46×10^{16}
	3	487	3.74×10^{19}	17.2×10^{19}
	4	544	13.8×10^{2}	1.39×10^{23}
3000 Gy	1	398	2.14×10^{15}	40.5×10^{15}
	2	412	8.00×10^{16}	55.5×10^{16}
	3	498	1.10×10^{17}	2.09×10^{17}
	4	552	3.45×10^{16}	1.52×10^{16}
2000 Gy	1	398	6.32×10^{12}	56.3×10^{12}
	2	409	2.86×10^{18}	2.20×10^{18}
	3	500	2.83×10^{18}	1.55×10^{18}
	4	550	1.56×10^{18}	2.42×10^{18}
1000 Gy	1	398	0.41×10^{14}	15.9×10^{14}
	2	409	27.7×10^{17}	7.13×10^{17}
	3	502	3.07×10^{16}	2.26×10^{16}
	4	548	3.55×10^{15}	2.75×10^{15}

2. CONCLUSION

In this work thermoluminescence study of $Sr_3B_2O_6:Sm^{3+}$ nanocrystalline phosphor prepared by combustion method exposed to different γ -dose ranging from 1000Gy -5000Gy has been presented. There is a significant variation in the glow curve peaks as its intensity increases with the increase in dose. It has been observed that on increasing y-dose from 1000Gy to 5000Gy, number of luminescent center in Sm³⁺ doped Sr₃B₂O₆ nanocrystalline phosphor increases, this is concluded from the observation that as the peak intensity in glow curve increases with increase in dose. The TL dose response is found to be linear in nature. Thus easy method of preparation, linear response over a range of exposure is some of the hall marks of the presented nanocrystalline phosphor. The kinetic parameters such as activation energy (E), order of kinetics (b) and frequency factor (s) of Sm^{3+} doped $Sr_3B_2O_6$ nanocrystalline phosphor irradiated with a γ -dose using ⁶⁰Co source ranging from 1000 Gy - 5000 Gy determined by TLAnal program and Chen's method are found to be in good agreement with each other.

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