THERMOLUMINESCENCE ANALYSIS AND CALCULATION OF TRAPPING PARAMETERS OF $SrZnF_4:Dy^{3+}$PHOSPHOR

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Abstract

Wet chemical method was employed to synthesize SrZnF4:Dy3+phosphors with 0.05, 0.1, 0.2, 0.5 and 1 mol% doping concentrations of Dy3+ ions. Thermoluminescence (TL) properties of prepared phosphors were studied by irradiating it with γ-rays from 60Co source. TL was obtained by irradiating phosphor with different doses of γ-rays and its linearity was checked over high dose of γ-ray radiation. Fading characteristic of the phosphors was studied by storing it for 10 days and reusability was checked for number of cycles. TL kinetic parameters such as order of kinetics, activation energy and frequency factors were calculated for different concentrations of Dy3+ ions and different γ-ray doses.

Keywords:SrZnF4; thermoluminescence (TL); trapping parameters; wet chemical synthesis.

1. INTRODUCTION

Rare earth doped inorganic materials are highly studied for their luminescence properties. They are having wide range of applications in lighting, display, dosimetry and medical field [1–3]. Rare earth doped phosphor possess thermoluminescence (TL) emission which is utilised for medical and environmental radiations dosimetry. TL phenomenon has been known for a long time and its first application for dosimetric purposes was from the work of Daniel et al. [4]. TL is the phenomenon of emission of light after heating a material which was previously irradiated with high energy ionizing radiations. Lots of research has been undertaken by the researchers for better understanding of TL phenomenon and improvement of material characteristics [5]. Nowadays, TL dosimetry (TLD) is a very well established dosimetry technique that finds application in diverse areas such as personal, environmental and clinical dosimetry. The materials which (after exposure to ionizing radiations) emit light when heated form the basis of TL dosimeters [6]. Impurities present in the material are believed to give rise to localized energy levels within the forbidden energy gap which store the energy from radiation and are crucial to the TL process. There is large number of materials which shows TL emission but it is not necessary that all these materials are useful for dosimetry purpose. Simple glow curve, High sensitivity; linear dose response, tissue equivalence, reusability; no fading; physical forms (loose powders or solid pieces) are some of the basic requirements for materials in order to use that material as a TL dosimeters in various field [7]. It is very difficult to synthesise or to discover a single material with all such required characteristics, and therefore, several material have been considered as TL dosimetry phosphors (TLDs) compromising on some or the factor [8] .

The TL properties of sulphate and lithium based phosphors activated by different rare earths have been studied intensively for many years and have resulted in a variety of applications [9,10]. The TL materials based on $CaSO_4$ have been widely used for environmental dosimetry and LiF doped with Mg and Ti is used for medical dosimetry due to its low tissue equivalency [10,11]. Fluoride based phosphors are highly studied for their excellent thermoluminescence properties for radiation dosimetry purpose. Fluorides have glow peak at high temperature range which ensures long lasting storage of TL. LiF and CaF_2 are readily used in dosimetry due to simple glow structure and high sensitivity [12,13]. In this paper, we have selected Strontium zinc fluoride ($SrZnF_4$) as a host material for the synthesis of phosphor. Crystal structure of $SrZnF_4$ compound was reported by Schneringet. al. [14]. $SrZnF_4$ compound hasScheelite-type structure with tetragonal unit cell. $SrZnF_4:Dy^{3+}$ phosphor is prepared by the wet chemical synthesis. Its photoluminescence and TL properties after β-ray irradiation are already reported in our previous research article [15]. Its TL response to γ-rays has been studied in detail in this work. Trapping parameters, dose response, fading and reusability of the $SrZnF_4$: Dy^{3+} phosphor also have been investigated in this study.

2. EXPERIMENTAL

$SrZnF_4:Dy^{3+}$ phosphors were prepared by simple wet chemical method. AR grade $SrCl_2$, $ZnCl_2$, NH_4F and Dy_2O_3 were taken as starting materials. Stoichiometric amounts of $SrCl_2$, $ZnCl_2$ and NH_4F were dissolved separately in double distilled de-ionized water. The dopant Dy_2O_3 was also taken in stoichiometric ratio, dissolved in few drops of Conc. HNO_3 acid, to convert it into water soluble nitrate form. All the solutions were poured into each other and heated at about 50 - 60 ˚C for 15 min. The compound $SrZnF_4$: Dy^{3+} in its powder form was obtained by evaporating solution 80 ^{0}C for 6-8 hours. The dried samples were then slowly cooled at room temperature. Details of this synthesis are also discussed by Shelkeet. al.[15] The resultant polycrystalline mass was crushed to fine particle in a mortar with pestle which was then used in further study.TL glow curve of the $SrZnF_4:Dy^{3+}$ phosphor was recorded using Thermoluminescence reader (Integral PC Based) Nucleonix - (TL-1009I) from room temperature to 300°C. For the TL measurement samples were exposed to γ-rays from ^{60}Co source at room temperature at the 0.45 kGy/hrate. After desired exposure, 5 mg of sample was taken each time and TL glow curve was recorded at a heating rate of 5˚C/s. The TL glow curves were recorded with the usual set-up consisting of a small metal plate heated directly using a temperature programmer, photomultiplier tube, dc amplifier and millivolt recorder.

3. RESULTS AND DISCUSSION

3.1 Thermoluminescence study

Fig. 1 shows the TL glow curves of γ-ray irradiated $SrZnF_4:Dy^{3+}$ sample at 3.6 kGy dose for different concentrations of Dy^{3+} ions. Two TL peaks are observed, one peak is present at around 182 ˚C (455 K) and other at around 253 °C (526 K) indicating the two set of traps are activated within the particular temperature range. The concentration dependence of TL glow curves of $SrZnF_4:Dy^{3+}$ phosphors with different Dy^{3+} concentrations are shown in Figure. TL intensity of glow curve goes on decreasing with increase in concentration of Dy^{3+} ions. The maximum intensity is observed for 0.05 mol% concentration of Dy^{3+} ion. The shape and the position of the TL peaks remain almost constant for all the concentrations. However, it shows that the intensity of the TL peak varies with the concentration of dopant.

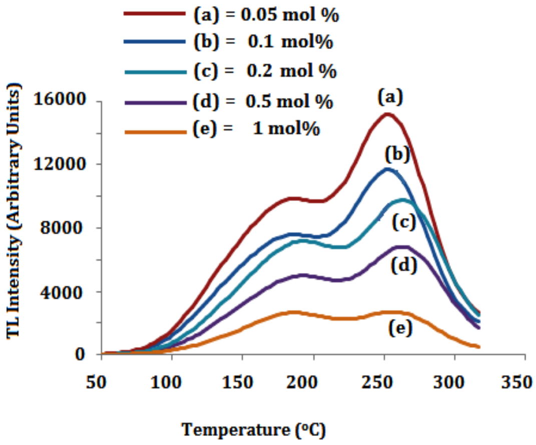

Fig. 1: TL glow curves of $SrZnF_4:Dy^{3+}$ phosphor exposed to γ-rays of 3.6 Gy dose from ^{60}Co source.

3.2 Role of different doses of γ-rays

Fig. 2 shows the TL glow curve for γ-ray irradiated $SrZnF_4:Dy^{3+}$phosphor with varying doses and linear heating rate. TL glow curve exhibits two glow peaks at 182 °C (455 K) and 253 °C (526 K). Figure shows that the TL intensity increases with the increase in dose and this change in the relative intensity of the glow peaks can be attributed to the change in the population of the luminescent or the trapping centres.

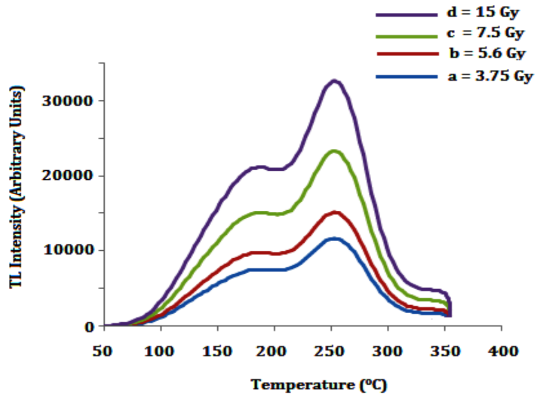

Fig. 2: TL glow curves of $SrZnF_4:Dy^{3+}$ (Dy^{3+} = 0.1 ml%) phosphor exposed to γ-rays for different doses.

3.3 Linearity, Fading and reusability

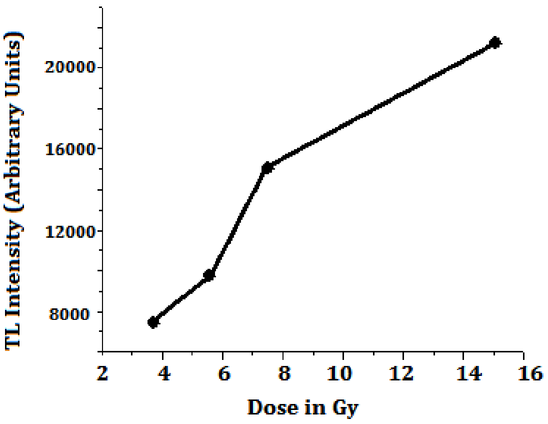

Fig. 3: TL response of $SrZnF_4:Dy^{3+}$ phosphor to γ- ray irradiation.

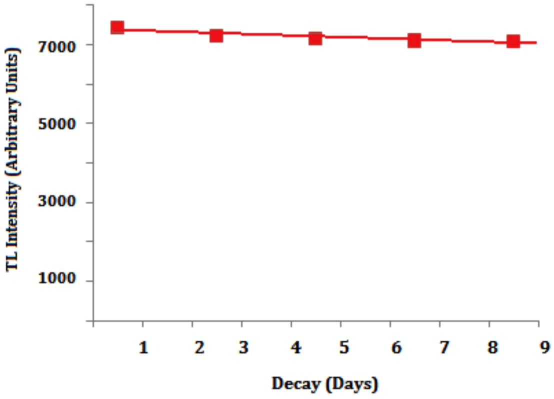

Fig. 4: Fading characteristic of $SrZnF_4:Dy^{3+}$ phosphor.

The TL response curve of $SrZnF_4:Dy^{3+}$ phosphor exposed to different doses of γ-rays is given in **Fig. 3**. The peak heights were used for measuring the TL intensities. Figure shows that the prepared phosphor exhibits nearly a linear response to γ-rays. The stability of the stored sample at normal temperatures is an important characteristic of TL materials in geological dating, personal and environmental dosimetry. In order to check the stability of the $SrZnF_4:Dy^{3+}$ for over 10 days by stores the samples without caring for the room temperature. The fading curve is shown in **Fig. 4**. There was just 5% fading over a period of 10 days suggesting no significant fading problem. For the radiation dosimetry, TL of the sample should be stable. If the sensitivity of a sample does not change after several cycles of exposures suggests that it is a good TL phosphor. The $SrZnF_4:Dy^{3+}$ was also tested for reusability. Several cycles of exposures and glow curve recordings were performed. No significant change in the intensities of peaks was observed.

3.3Trapping parameters

The TL glow curve provides information about the nature of traps present in the TL material and the amount of energy absorbed by the incident radiation in the material. The study of kinetic parameters, including activation energy (E) and frequency factor (s) is considered as an important aspect of TL because it provides information about the defect centers responsible for the TL. Activation energy is also called as trap depth, where charges get trapped after irradiation. Frequency factor gives the number of attempts in getting detrapped from particular trap by electrons. Order of kinetics is the mechanism by which electron gets release from the defect level and get recombine at recombination centre [16].

TL glow peak, in general, consist of number of overlapping peaks of different order and corresponds to traps present at different energies. To determine the various trapping parameters associated with TL glow peak, we need to separate or isolate this TL peaks. By analysing isolated TL peaks, trapping parameters can be determined. TL glow curve with complex glow curve structure containing more than one peak, can be deconvoluted and fitted theoretically using glow curve deconvolution (GCD) method [17]. Thermal cleaning process can be employed to determine peak position of overlapped peaks and then by giving rough estimate of E and b values, glow curves are fitted by using Kitis first, second and general order equation [18], given below

For first order,

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

For second order,

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

For general order,

$$I(T) = I_m b^{\left(\frac{b}{b-1}\right)} \exp\left\{\left(\frac{E}{kT}\right)\frac{T-T_m}{T_m}\right\} \times \left[(b-1)\left(1 - \frac{2kT}{E}\right)\left(\frac{T^2}{T_m^2}\right)\exp\left\{\left(\frac{E}{kT}\right)\frac{T-T_m}{T_m}\right\} + 1 + (b-1)\frac{2kT_m}{E}\right]^{-\left(\frac{b}{b-1}\right)} \quad (3)$$

where, T_m (K) is the peak temperature, I (T) is the TL intensity at temperature T (K), I_m is the maximum peak intensity, E (eV) is the activation energy, k is the Boltzmann constant, b is order of kinetics. This procedure of theoretical fitting of glow curve is repeated for the TL peaks till a theoretical glow curve best fitted with experimental one. Measure of the goodness-of-fit can be obtained by figure of merit (FOM) and it is given

$$FOM = \frac{\sum_i |TL_{exp} - TL_{fit}|}{\sum_i TL_{fit}}$$

where, TL_{exp} and TL_{fit} represent the experimental TL intensity data and the value of the fitting function, respectively [19]. Values of FOM in between 1 to 5 represent a good fit of TL glow curve. The frequency factor (s) can be calculated using equation (4) given below, by substituting the value of E and b.

$$\frac{\beta E}{kT_m^2} = s \exp\left(\frac{-E}{kT_m}\right)\left[1 + (b-1)\Delta_m\right] \quad (4)$$

where, $\Delta_m = 2kT_m/E$, b is the order of kinetics, k is the Boltzmann constant and β is the linear heating rate (5 °C/s).

By applying above method trapping parameters were calculated for γ-ray irradiated $SrZnF_4:Dy^{3+}$ phosphor doped with different concentration of Dy^{3+} ions as shown in **Fig. 5**. Figure shows experimental, deconvoluted and theoretically fitted TL glow curve of $SrZnF_4:Dy^{3+}$ (Dy^{3+} = 0.05, 0.1, 0.2, 0.5 and 1 mol%) phosphor. All the TL curves consist of three overlapping peaks which represents presence of three types of defect energy levels. All the three TL glow curves follow second order kinetics and their activation energies and other parameters are tabulated in Table 1. Lower temperature side peak has activation energy value as 0.6 eV and higher temperature side peak has activation energy as 1.2 eV. Frequency factor shows increase from lower temperature side to higher temperature side. Trapping parameters of $SrZnF_4:Dy^{3+}$ (0.1 mol %) phosphor irradiated with different γ-ray doses were calculated and values are given in Table 2. With different irradiation doses number of TL glow peaks remains same as shown in **Fig. 6** which indicates the same types of defects generation for various doses.

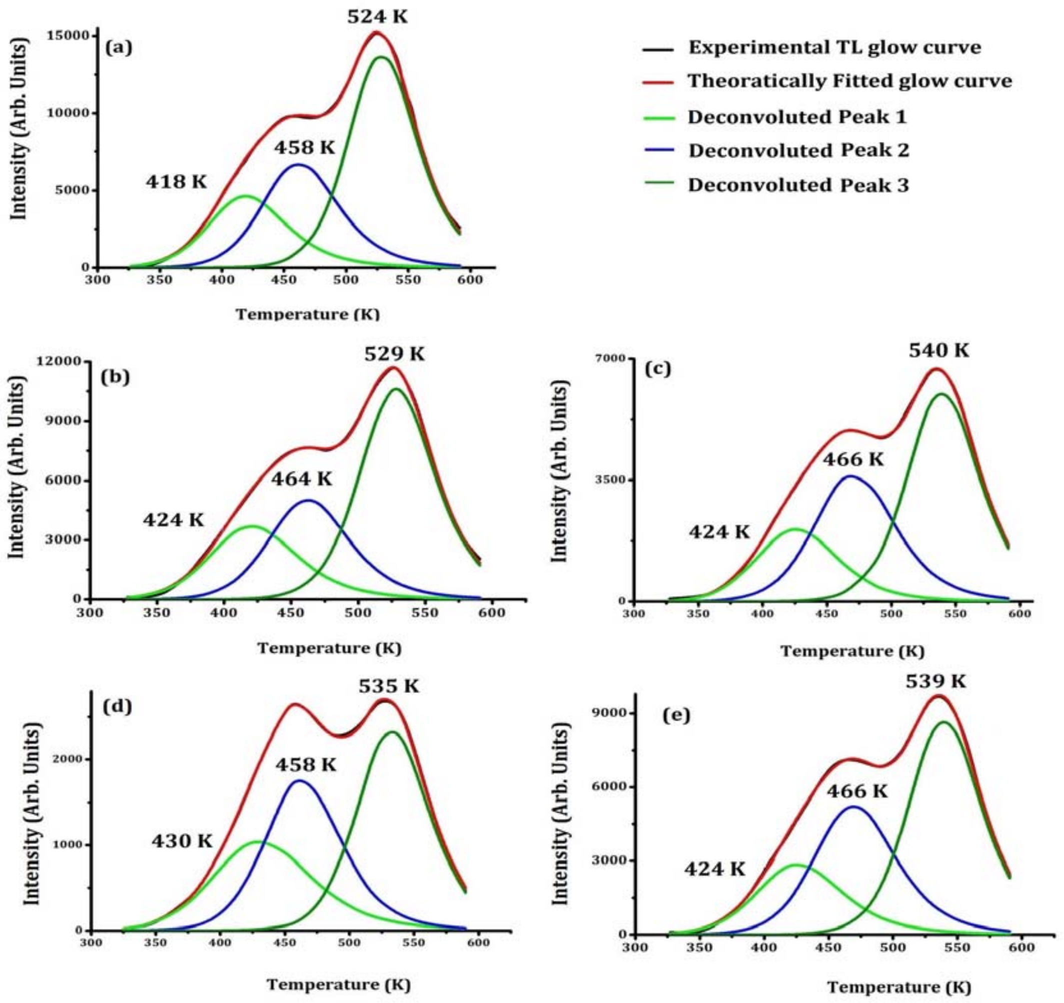

Fig. 5: Glow curve deconvolution (GCD) of SrZnF4:Dy^{3+} phosphor irradiated with 3.75 Gy of γ-rays. (a) Dy^{3+} = 0.05 mol%, (b) Dy^{3+} = 0.1 mol%, (c) Dy^{3+} = 0.2 mol%, (d) Dy^{3+} = 0.5 mol%, (b) Dy^{3+} = 1 mol%.

Table 1: Trapping parameters of SrZnF$_4$:Dy^{3+} phosphor irradiated with γ-rays of 3.75 Gy dose

Dy^{3+} concentration (mol %)	Peak Temperature (T_m) (K)	Peak Intensity (I_m) (Arb. Units)	Order of kinetics (b)	Activation energy (E) (eV)	Frequency factor (S) (s^{-1})	FOM
0.05	418	4638	2	0.6552	191.05	1.156%
	458	6751	2	0.8287	2067.22	
	524	13696	2	1.2111	408432.83	
0.1	424	3743	2	0.6491	182.81	1.233%
	464	5081	2	0.8605	6538.28	
	529	10671	2	1.2057	473536.73	
0.2	424	2181	2	0.6439	153.12	1.203%
	466	3757	2	0.8400	2452.21	
	540	6100	2	1.2520	889966.19	
0.5	430	1076	2	0.7169	1876.03	1.306%
	458	1782	2	0.8715	7539.59	
	535	2390	2	1.2685	1877352.83	
1	424	2874	2	0.5820	50.83	1.334%
	466	5302	2	0.8964	47342.182	
	539	8815	2	1.2806	9245925.93	

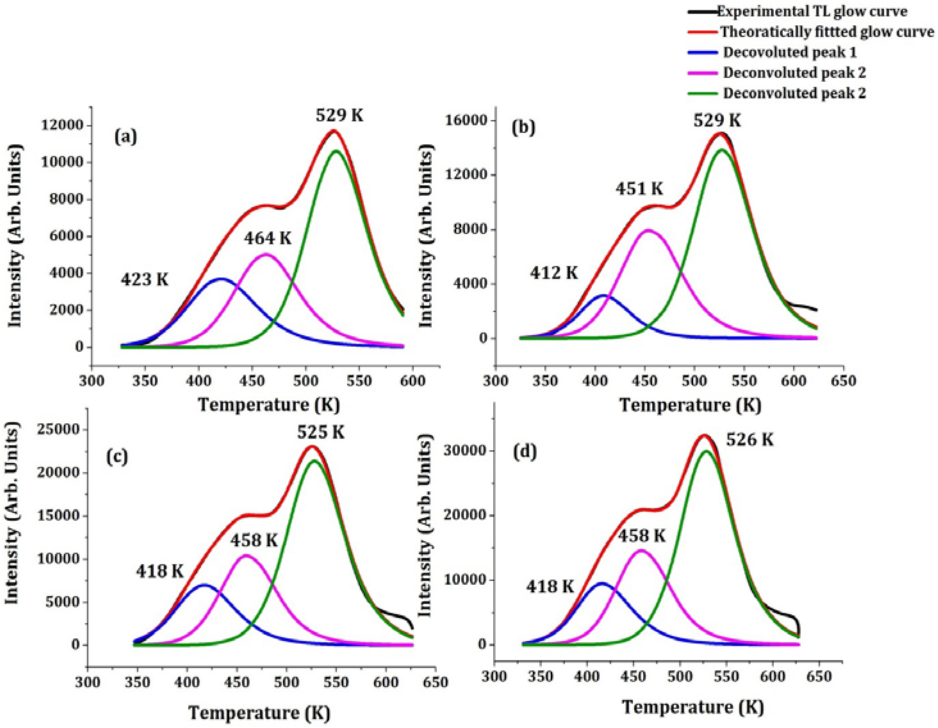

Fig. 6: Glow curve deconvolution (GCD) of $SrZnF_4:Dy^{3+}$ (Dy^{3+} = 0.1 mol%) phosphor irradiated with of γ-rays. (a) 3.75 Gy (b) 5.7 Gy (c) 7.5 Gy (d) 15 Gy.

Table 2: Trapping parameters of $SrZnF_4:Dy^{3+}$ (Dy^{3+} = 0.1 mol%) phosphor irradiated with different doses of γ-rays

Irradiation Dose (Gy)	Peak Temperature (T_m) (K)	Peak Intensity (I_m) (Arb. Units)	Order of kinetics (b)	Activation energy (E) (eV)	Frequency factor (S) (s^{-1})	FOM
3.75	424	3743	2	0.6491	182.81	2.998%
	464	5081	2	0.8605	6538.28	
	529	10671	2	1.2057	473536.73	
5.6	412	2791	2	0.8274	100341.87	2.752%
	451	8181	2	0.8233	2150.80	
	529	13903	2	1.1453	88894.35	
7.5	418	7206	2	0.7074	683.04	2.921%
	458	10787	2	0.9261	20334.41	
	525	21493	2	1.1681	96124.25	
15	418	9543	2	0.7032	462.80	2.476%
	458	15116	2	0.8826	4758.78	
	526	30141	2	1.1648	62656.15	

4. CONCLUSION

The SrZnF4:Dy3+ phosphor was synthesized by the wet chemical method and characterized for its TL emission after γ-ray irradiation. From TL studies, it is observed that the sensitivity of SrZnF4:Dy3+ phosphor is high. The trapping parameters of SrZnF4:Dy3+ phosphor calculated by GCD method for different concentration and different γ-ray dose. All the TL curves consist of three peaks and follows second order kinetics. Easy method of preparation, good sensitivity, linear response and good reusability are some of the noble features of the presented phosphor which will make it useful for its applications in radiation dosimetry.

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