Kinetic Analysis of TL Spectrum of ϒ-Irradiated$SrAl_2O_4:Eu^{2+}$, Dy^{3+} Nanophosphor

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Abstract- **Thermoluminescence is a simple technique for studying the distribution of artificially created or naturally occurring point defects. In present work we are reanalyzing the Thermoluminescence response of Eu^{2+},Dy^{3+} doped $SrAl_2O_4$ nanophosphor at different irradiation dose of ϒ-rays, in accordance with new method of analysis. Orders of kinetics for different glow curves are recalculated. Order of kinetics values are not same as already reported in literature. As per new model order of kinetics depends on extent of retrapping and from reanalysis we can infer that all the reported TL responses of material under consideration are retrapping dominant process.**

Keywords- **Thermoluminescence, Orders of kinetics, Glow Curves, Irradiation Dose, Retrapping.**

I. INTRODUCTION

Phosphor is luminescent material that emits light when exposed to radiation such as ϒ- ray,ultraviolet light, visible, infrared radiation or an electron beam. Thousands of phosphors have been synthesized, each one having its own characteristic colour of emission and period of time during which light is emitted after excitation ceases. Phosphors excited by ultraviolet, visible, and infrared radiation are used principally in the fluorescent lamps commonly employed for general illumination. Thermoluminescence (TL) is emission of light from some minerals and certain other crystalline materials. The light energy released is derived from electron displacements within the crystal lattice of such a substance caused by previous exposure to high-energy radiation. Heating the substance in suitable temperature range enables the trapped electrons to return to their normal positions, resulting in the release of energy. The intensity of the emission can be correlated to the length of time that a given substance was exposed to radiation; the longer the time allowed for the radiation to build up an inventory of trapped electrons, the greater the energy released. Because of this feature, thermo luminescence has been exploited as a means of dating, dosimetry and characterization of luminescent material. In the structure of the inorganic phosphors there exist point defects, naturally occurring or artificially created, which induce electronic states in the forbidden band; these defects have great importance on understanding the TL phenomenon [1-5]. It is a simple, efficient, convenient and relatively inexpensive experimental technique to study various aspects of the role of defects and impurities in solids with considerably reliability [6-8]. The polycrystalline materials exhibit a glow curve with one or more peaks when the trapped electrons are released and then captured by luminescence centers by thermal stimulation. This glow curve, also known as TL spectrum or Thermogram, is a graphical representation of the luminescence intensity as a function of temperature, providing information about decay parameters , such as activation energy (E_a), frequency factor (s) and the order of the kinetics (ℓ) [9-12]. TL response depends strongly on the material, the type of impurity, radiation induced defect centers, dose and type of ionizing radiation [13-22]. As the TL intensity is related to the radiation dose, TL is widely used in radiation dosimetry and in geological dating [23]. Because of high demand of sensitive TL dosimetry phosphors numerous research work carrying regularly on different phosphor materials. Due to long duration phosphorescence characteristics and high quantum efficiency $SrAl_2O_4$ doped with different materials are widely studied [24-27].

In this paper, we reconsider the results of TL response of $SrAl_2O_4$: Eu^{2+}/Dy^{3+} phosphors, already reported in literature by Bedyal et. al. [28], as per the new method of analysis for re-evaluation of order of kinetics and extent of retrapping which helps in ascertaining the materials capability for usage as high gamma dose dosimeter for industrial and scientific applications.

II. MATERIAL AND METHOD OF ANALYSIS

Aluminum nitrate [$Al(NO_3)_3$], Europium nitrate [$Eu(NO_3)_3$], Dysprosium nitrate [$Dy(NO_3)_3$], and Urea (NH_2NCONH_2) of analytical regent grade were used as the initial materials by Bedyal et. al. [28]. For preparation Strontium aluminates by combustion method [28] stoichiometric composition of the metal nitrate (oxidizer) and urea (fuel) was calculated based on the total oxidizing and reducing valency of the oxidizers, such that oxidizer and fuel ratio is unity i.e. O/F = 1 in order to have the energy released as a maximum for complete combustion. The calculated amount of metal nitrates and urea were dissolved into the smallest possible amount of distilled

water and thoroughly mixed in a mortar to obtain a homogeneous mixture. The mixture was then transferred to an alumina crucible and inserted into a pre-heated muffle furnace maintained at 550 °C. The reaction began within a few minutes after the introduction of the crucible into the furnace. The mixture was then self-ignited with a white flame and yields highly porous foamy solid product. After the completion of the reaction, the foamy product was cooled to room temperature and finally crushed to the fine powder with the help of a mortar and pestle. The fine powder was then calcined at 800°C for two hours to get complete crystallinity. The structural characterization of the samples was carried out by X-ray powder diffraction (XRD) and morphology and sizes of the product were verified by Transmission Electron Microscope [28]. The prepared samples were exposed to ϒ-radiation at room temperature with different doses, by using a gamma chamber. The TL glow curves of the exposed nanophosphors were recorded on HARSHAW QS 3500 TLD reader, with linear heating rate of, 5^0K/s, taking 5 mg of samples each time by Bedyal et. al. [28].

To analyze the recorded glow curves of $SrAl_2O_4$: Eu^{2+}, Dy^{3+} nanophosphors, the *TL Anal* program developed by Chung *et al* [29] was used for glow curve deconvolution. Chen formulism [30] has been used by Bedyal et. al. [28] to calculate, decay parameters like activation energy (E_a) , frequency factor (*s*) and the order of the kinetics (ℓ) for each of the deconvoluted peak of the prepared phosphors exposed at room temperature with different ϒ- radiation dose.

III. RESULTS AND DISCUSSION

The recorded glow curves of the prepared $SrAl_2O_4$: Eu^{2+}, Dy^{3+} phosphors exposed to ϒ-radiation (20Gy - 800 Gy) by Bedyal et. al. [28] are shown in Fig.1. From obtained glow curve it is clear that for each radiation dose, there is more than one peak and they are not clearly resolved. For the purpose of evaluation of decay parameters it is necessary to resolve these peaks. Bedyal et. al. [28] resolved these peaks by Computer Deconvolution TL Anal programme developed by Chung *et al* [29]. Such Deconvoluted glow curve for radiation dose 800 Gy is shown in Fig.2. With the help of Chen's method [30], decay parameters are calculated by Bedyal et. al. [28] and are given in Table.1.

There are so many mechanisms and theory reported in literature for the appearance of TL glow curve. In most of the theory condition for peak temperature is given by relation as below

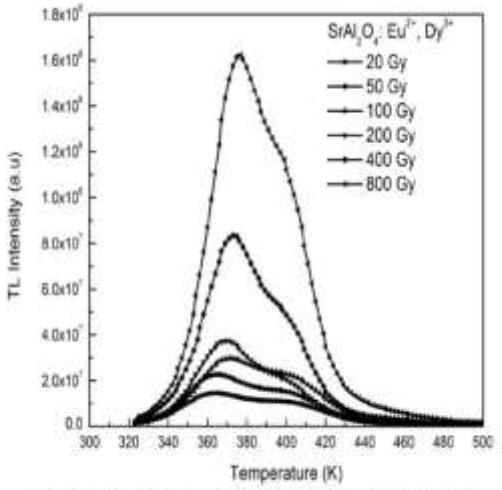

Fig.1 Glow Curves of $SrAl_2O_4$: Eu^{2+}, Dy^{3+} nanophosphor at different doses of Y-radiation [28].

$$T_m^2 = \frac{b\,E_a \tau_m}{k} \qquad (1)$$

where T_m is peak temperature, b is linear heating rate, τ_m is relaxation time at peak temperature and is given by S. Z. Arrhenius [31] as

$$\tau_m = \tau_0 \exp\left(\frac{E_a}{k\,T_m}\right) \qquad (2)$$

where τ_0 is fundamental relaxation time (inverse of frequency factor) and k is Boltzmann's constant. All the decay parameters and corresponding peak temperature values must have to satisfy the peak temperature relation (1). The values of T_m^2 and $\frac{b\,E_a\,\tau_m}{k}$ are calculated and given in Table.1. From columns five and six of this table it is clear that eq.(1) is not satisfied. In order to remove this shortcoming here we apply a new method of analysis suggested by Prakash [32] and Prasad et al [33] to calculate order of kinetics and extent of retrapping involved in TL glow curves of $SrAl_2O_4$: Eu^{2+}, Dy^{3+}.

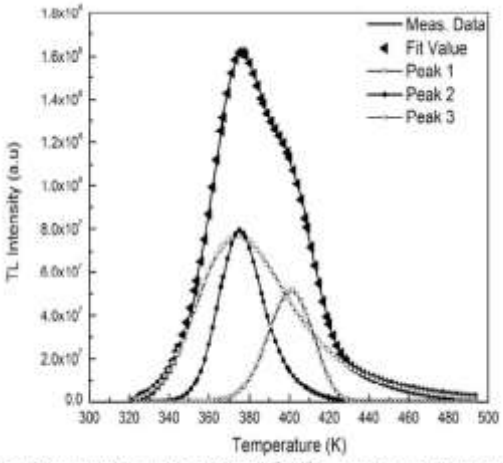

Fig.2 The Deconvoluted glow curve fitting of $SrAl_2O_4$: Eu^{2+}, Dy^{3+} nanophosphor irradiated with ϒ-radiation of 800 Gy [28].

Table.1

Reported values of Activation Energy, Frequency Factor and calculated values of Order of Kinetics with extent of Retrapping.

E_a (eV)	s (s^{-1})	τ_0 (s)	T_m (^{0}K)	T_m^2 ($^0K^2$)	$\frac{b E_a \tau_m}{k}$ ($^0K^2$)	ℓ	x
0.8729	2.00E+13	5.00E-14	365	133225	2862.059	46.54865	0.978517
1.9606	2.70E+26	3.70E-27	397	157609	3271.471	48.1768	0.979243
1.9165	8.20E+24	1.22E-25	413	170569	3311.164	51.51331	0.980588
1.2691	5.80E+18	1.72E-19	369	136161	2739.29	49.70667	0.979882
0.566	5.00E+08	2.00E-09	373	139129	2919.093	47.66172	0.979019
1.3302	9.90E+17	1.01E-18	403	162409	3369.448	48.20048	0.979253
0.7689	4.90E+11	2.04E-12	370	136900	2709.547	50.52506	0.980208
1.5131	9.60E+21	1.04E-22	372	138384	2891.781	47.85425	0.979103
1.7649	6.00E+23	1.67E-24	399	159201	3353.802	47.46881	0.978934
0.8533	5.60E+12	1.79E-13	374	139876	2789.217	50.14884	0.980059
1.6711	1.00E+24	1.00E-24	375	140625	2793.061	50.34798	0.980138
1.5899	2.90E+21	3.45E-22	400	160000	3429.405	46.65532	0.978566

In new method equation for TL intensity and peak temperature are given by following relations

$$I = (1-x)n_0 s \exp[\left(-\frac{E_a}{kT}\right) - \frac{s\,(1-x)}{b}\int_{T_0}^{T} \exp\left(-\frac{E_a}{kT'}\right)dT'] \qquad (3)$$

and

$$T_m^2 = \frac{\ell\, b\, E_a \tau_m}{k} \qquad (4)$$

where I is TL intensity at temperature T, x is extent of retrapping, n_0 is the initial concentration of trapped carriers per unit volume, T_o the temperature at which TL glow curve starts to appear, T′ any arbitrary temperature in the range T_o to T. Extent of retrapping is related with order of kinetics ℓ as

$$\ell = \frac{1}{1-x} \qquad (5)$$

As per this new method of analysis order of kinetics ℓ and extent of retrapping x is evaluated and presented in seventh and eighth columns of Table.1 respectively. From reported TL spectrum it is clear that peak starts shifting towards the higher temperature as the exposed dose increased.

The emission peak temperature was found to shift towards a high temperature as the dose increased which could be attributed to the creation of deep level defects caused by irradiation [34,35].

IV. CONCLUSION

Thermoluminescence studies on nanostructure of $SrAl_2O_4$: Eu^{2+}, Dy^{3+} phosphor irradiated with gamma rays is reconsidered here in light of new method of analysis. Order of kinetics and extent of retrapping for this sample at a linear heating rate of 5 K/s is recalculated according to this new approach. The results are different from earlier reported results. All the thermoluminescence spectrums are retrapping dominant processes. The emission peak current increases with increase in radiation dose, which is in agreement with new approach of analysis but shift in peak temperature with radiation dose is a new observation which may be due to nanostructures. Correct knowledge of decay parameters and order of kinetics or extent of retrapping are helpful in selecting the nanophosphor for different uses like in display devices, in dosimetry and in TL dating material.

ACKNOWLEDGEMENTS

The author is thankful to the Director of his institute for providing the facilities and also thankful to Prof. Jai Prakash, Ex Pro Vice Chancellor, Pt. D D U Gorakhpur University, Gorakhpur for inculcating research temper.

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