Doping Concentration and T L Behaviour of Materials

by

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Abstract

Thermoluminescence behaviour of materials is affected by adding dopant and also by its concentration. Mostly this affects the peak intensity of glow curve. In present study various experimentally reported glow curves of different materials are reanalyzed in respect of variable concentration of doping. Number of luminescence centers and hence area under glow curve increases with doping concentration and reaches a maximum value then decreases. Present study rigorously analyzes this and also evaluates decay parameters, order of kinetics and extent of retrapping in view of different doping concentration.

Keywords*: Thermoluminescence, Glow curve, Dopant, Concentration quenching, Phosphor.*

Introduction:

Thermoluminescence (TL) and other luminescence effects in materials are directly related to the imperfections inside it. These imperfections are impurities, defects etc. Thermoluminescence (TL) of phosphor materials generally exhibit complex nature in respect of peaks when the charge carriers are released from respective trap levels. Trap levels in the band gap of materials are characterized by decay parameters namely, activation energy (E_a) and escape frequency factor (s). For TL applications appropriate knowledge of these parameters along with order of kinetics is essential. Because of high chemical stability, long life and bright emission characteristics etc [1-6] rare earth activated aluminate based phosphors have been extensively investigated. Researchers have also keen interest in rare earth activated phosphors due to wide applications in display device material as used in high definition (HD), projection televisions (PTVs), and flat panel displays (FPDs).

The present work took a small step to understand the variation in TL behavior, decay parameters and order of kinetics in respect of different concentrations of doping. For this purpose present study extensively reconsider the already reported experimental glow curves of different phosphor materials.

Materials and Method of Analysis:

Present study considers experimentally reported glow curve of $BaAl_2O_4:Eu^{2+}$ phosphor, synthesized by the combustion method and is reported by Bhushan et.al.[7]. They irradiate material by electron beam and gamma rays are while performing TL measurements. Present study again consider the experimentally reported glow curve of $BaMgP_2O_7:Ce^{3+},Tb^{3+}$ with respect to different concentration of Ce^{3+} by J. A. Wani et.al.[8]. They prepare sample by solid state diffusion method and irradiated with γ- rays of 60Co source (dose =3 Gy) Fig.20. Thirdly glow curve of $Mg_5(BO_3)_3F:Dy^{3+}$ phosphor with varied concentrations of Dy^{3+} exposed to 8.3Gy of γ-irradiation at room temperature as experimentally reported by Wani et.al.[9] has been considered. The sample was prepared by modified solid state reaction method. Further study considers the effect of Eu^{3+} concentration on TL glow curve of Gd_2O_3: Eu^{3+} phosphor under 10 min UV exposures as reported by Raunak kumar Tamrakar et. al.[10]. The sample was prepared by the solid state reaction method.

The considered experimentally reported glow curves are reanalyzed by Prakash method [11]. According to this method TL intensity I is given by

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

where x is the extent of retrapping in T L process, n_o the initial concentration of trapped carriers per unit volume, s the escape frequency factor or pre-exponential factor, E_a the trap depth or activation energy, k the Boltzmann's constant, b the linear heating rate, T_o the temperature at which TL glow curve starts to appear and T' an arbitrary temperature in the range T_o to T. Temperature T_m at which peak of the T L spectrum appears is given by the relation [11]

$$T_m^2 = \frac{b\,E_a\tau_m}{(1-x)\,k} \quad \ldots (2)$$

where τ_m is the relaxation time at the peak temperature T_m. Relaxation time τ at any temperature T is given by Arrhenius relation [12]

$$\tau = \tau_0 \exp\left(\frac{E_a}{k\,T}\right) \quad \ldots (3)$$

where τ_0 is the fundamental relaxation time (inverse of escape frequency factor s such that $\tau_0 = \frac{1}{s}$). As per the Prakash [11] model n is the density of electrons in the trap centers at temperature T and n_0 is the initial concentration of the trapped electrons per unit volume at temperature T_0. The values of n and n_0 are given by the relations

$$n = \frac{1}{b}\int_{T}^{\infty} I(T')\, dT' \quad \ldots (4)$$

and

$$n_0 = \frac{1}{b}\int_{T_0}^{\infty} I(T')dT' \quad \ldots (5)$$

Based on the arguments proposed by Prakash [11] and Bucci et. al. [13] it is obvious that E_a and s of the system do not change due to different extent of retrapping. The evaluated values of E_a and s correspond to a case of zero retrapping in the system. Thus, the values of E_a and s can be obtained after substituting $x = 0$ in the relevant equations. In such condition, one of the modified Adirovitch set of equations

$$I = -\frac{dm}{dt} = (1-x)ns\exp\left(-\frac{E_a}{kT}\right) \quad \ldots(6)$$

where *m is* density of holes in recombination centre, changes into

$$I = ns\exp(-\frac{E_a}{kT}) \quad \ldots (7)$$

which can be rearranged as

$$\ln(\frac{n}{I}) = \ln(\frac{1}{s}) + \frac{E_a}{kT} \quad \ldots (8)$$

It is obvious from above equation that one gets a straight line when *ln (n/I)* is plotted against *(1/T)*. The slope of the line gives the value of activation energy E_a and from the intercept one gets the value of escape frequency factor *s*. By putting the values of E_a and s in equation (2), one gets the value of extent of retrapping $\boldsymbol{x}$ in corresponding TL process. Extent of retrapping $\boldsymbol{x}$ is related with the order of kinetics ℓ through the relation [19]

$$\ell = \frac{1}{1-x} \quad \ldots(9)$$

It is obvious that for x = 0, one gets the value of ℓ as 1. In such a case of x = 0, all the above equations become identical to corresponding equations of Bucci et.al. method [13].

Result and Discussion:

Prakash method of analysis has been applied on four different host materials. These host materials are activated by different concentration of foreign materials. For analysis study firstly considers experimentally reported T L glow curves of $BaAl_2O_4:Eu^{2+}$ phosphor [7] for different concentrations of Eu^{2+}. As per eq.(8) of the adopted method of analysis *ln (n/I)* is plotted against *(1/T)* for all the curves corresponding to different mol % of Eu^{2+}. A representative straight line plot corresponding to 1.0% mol concentration dose of Eu^{2+} is shown in Fig.1.

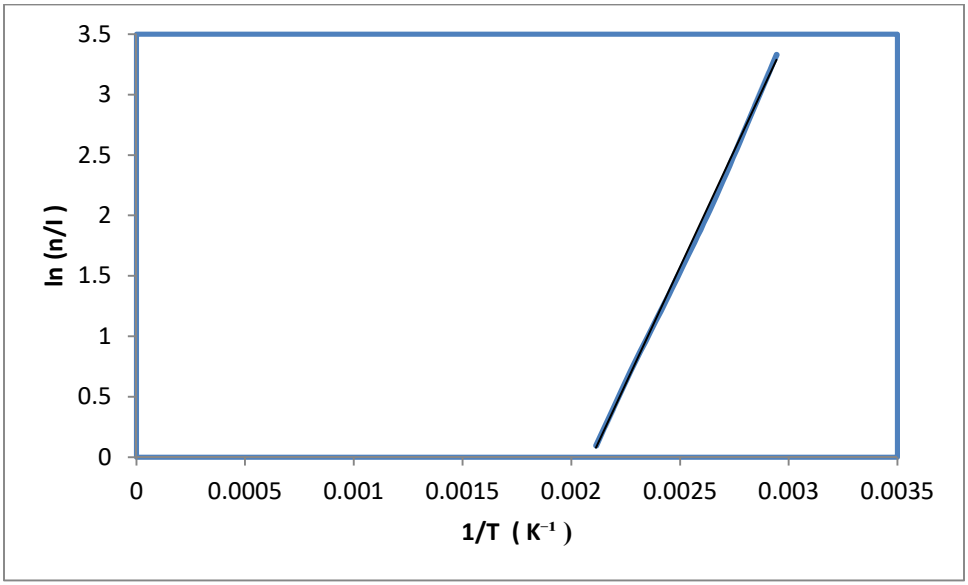

Fig.1 Plot of *ln(n/I)* vs *1/T* for 1.0 % mol Eu^{2+} glow curve of $BaAl_2O_4:Eu^{2+}$.

Slope of the straight line gives the value of activation energy E_a and the intercept results into escape frequency factor s. These evaluated values with the help of eqs.(2) and (9) give the values of extent of retrapping ***x*** and order of kinetics ℓ. These evaluated values for all the individual concentration curves and corresponding straight lines are presented in Table.1.

Table.1 Experimental and evaluated values of mol %, T_m, E_a, s, *x*, and ℓ for $BaAl_2O_4:Eu^{2+}$.

TL glow curve of	% mol of Eu^{2+}	T_m (K)	E_a (eV)	s (s^{-1})	*x*	ℓ
$BaAl_2O_4:Eu^{2+}$	0.2	429.7	0.34	1.60E+03	0.35	1.5
	0.5	419.7	0.42	2.30E+04	0.33	1.5
	1.0	419.7	0.33	3.30E+03	0.70	3.3
	0.1	419.7	0.34	3.80E+03	0.64	2.8
	0.05	423	0.36	7.60E+03	0.70	3.3

Secondly study considers experimentally reported T L glow curves of $BaMgP_2O_7:Ce^{3+},Tb^{3+}$ with respect to different concentration of Ce^{3+} [8]. As per eq.(8) of the adopted method of analysis *ln (n/I)* is plotted against *(1/T)* for all the curves corresponding to different mol % of Ce^{3+}. A representative straight line plot corresponding to 0.3% mol concentration dose of Ce^{3+} is

presented in Fig.2. And slope of the straight line gives the value of activation energy E_a and the intercept results into escape frequency factor s. These evaluated values with the help of eqs.(2) and (9) give the values of extent of retrapping ***x*** and order of kinetics ℓ. These evaluated values for all the individual concentration curves and corresponding straight lines are presented in Table.2.

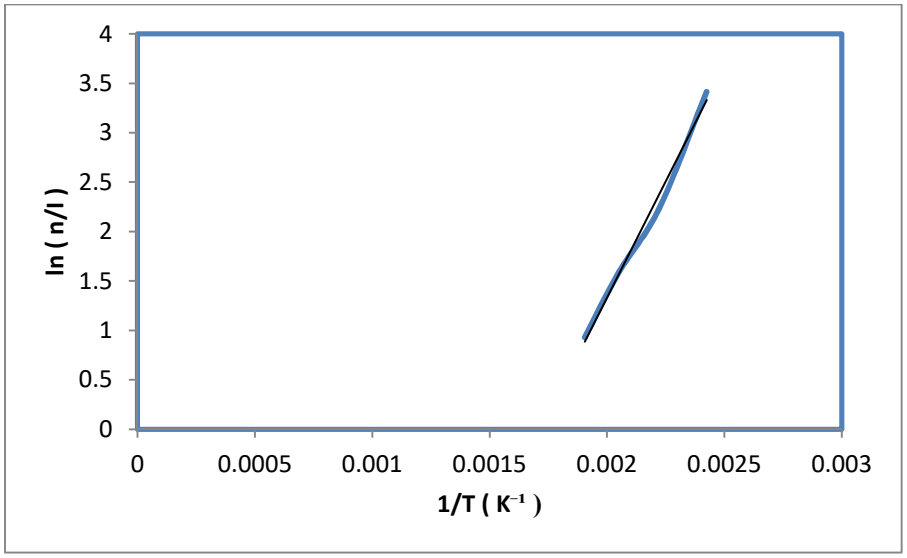

Fig.2 Plot of *ln(n/I)* vs *1/T* for 0.3 % mol Ce^{3+} glow curve of $BaMgP_2O_7:Ce^{3+},Tb^{3+}$.

Table.2 Experimental and evaluated values of mol %, T_m, E_a, s, *x*, and ℓ for $BaMgP_2O_7:Ce^{3+},Tb^{3+}$.

TL glow curve of	% mol of Ce^{3+}	T_m (K)	E_a (eV)	s (s^{-1})	*x*	ℓ
$BaMgP_2O_7:Ce^{3+},Tb^{3+}$	1.0	476.3	0.39	1.80E+03	0.70	3.4
	2.0	476.3	0.37	1.00E+03	0.69	3.2
	0.5	476.3	0.36	9.20E+02	0.74	3.9
	0.3	476.3	0.41	3.20E+03	0.71	3.5
	0.1	476.3	0.37	1.20E+03	0.74	3.9

Next glow curves of $Mg_5(BO_3)_3F:Dy^{3+}$ phosphor with varied concentrations of Dy^{3+} as experimentally reported by Wani et.al.[9] have been analyzed and analysis *ln (n/I)* is plotted against *(1/T)* for all the curves corresponding to different mol % of Dy^{3+}. A representative straight line plot corresponding to 0.1% mol concentration dose of Dy^{3+} is presented in Fig.3. And slope of the straight line gives the value of activation energy E_a and the intercept results into escape frequency factor s. These evaluated values with the help of eqs.(2) and (9) give the values of extent of retrapping ***x*** and order of kinetics ℓ. These evaluated values for all the individual concentration curves and corresponding straight lines are presented in Table.3.

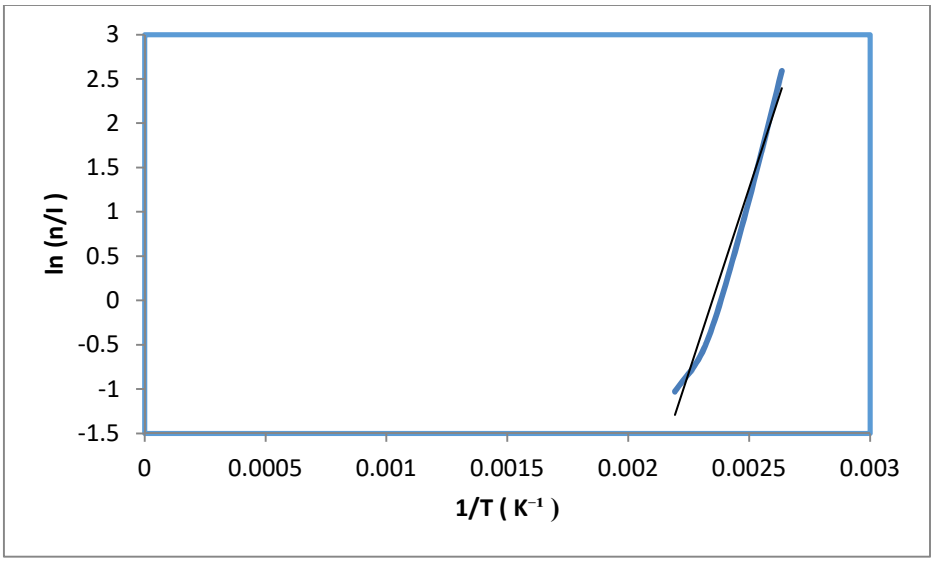

Fig.3 Plot of *ln(n/I)* vs *1/T* for 0.1 % mol Dy^{3+} glow curve of $Mg_5(BO_3)_3F:Dy^{3+}$.

Table.3 Experimental and evaluated values of mol %, T_m, E_a, s, *x*, and ℓ for $Mg_5(BO_3)_3F:Dy^{3+}$.

TL glow curve of	% mol of Dy^{3+}	T_m (K)	E_a (eV)	s (s^{-1})	*x*	ℓ
$Mg_5(BO_3)_3F:Dy^{3+}$	0.5	417.8	0.63	2.80E+07	0.40	1.7
	0.3	417.8	0.58	5.60E+06	0.32	1.5
	0.1	417.8	0.72	3.20E+08	0.27	1.4
	1.0	417.8	0.8	2.40E+09	0.01	1.0
	0.05	417.8	0.94	2.80E+11	0.51	2.1

In last glow curves of Gd_2O_3: Eu^{3+} phosphor for different doping concentration of Eu^{3+}, as reported by Tamrakar et. al.[10] have been analyzed and *ln (n/I)* is plotted against *(1/T)* for all the curves corresponding to different mol % of Eu^{3+}. A representative straight line plot corresponding to 1.0% mol concentration dose of Eu^{3+} is presented in Fig.4.

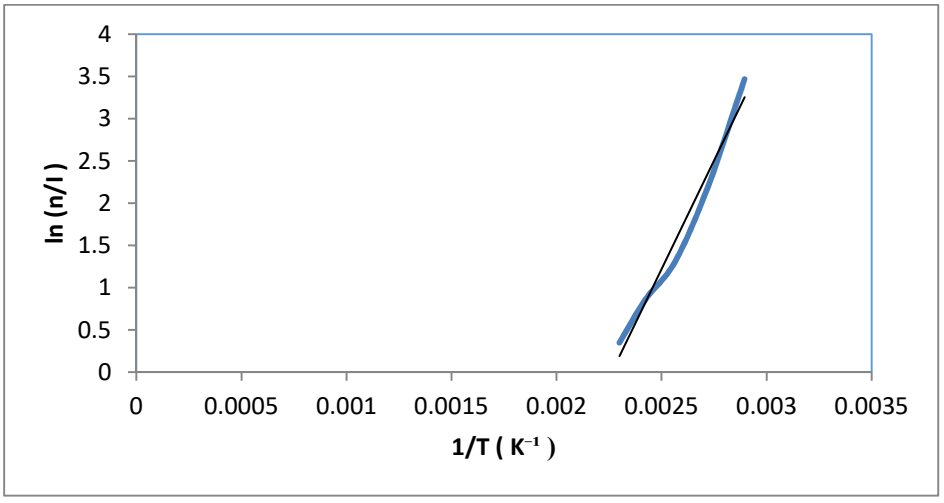

Fig.3 Plot of *ln(n/I)* vs *1/T* for 1.0 % mol Eu^{3+} glow curve of Gd_2O_3: Eu^{3+}.

And slope of the straight line gives the value of activation energy E_a and the intercept results into escape frequency factor s. These evaluated values with the help of eqs.(2) and (9) give the values of extent of retrapping x and order of kinetics ℓ. These evaluated values for all the individual concentration curves and corresponding straight lines are presented in Table.4.

Table.4 Experimental and evaluated values of mol %, T_m, E_a, s, x, and ℓ for Gd_2O_3: Eu^{3+}.

TL glow curve of	% mol of Eu^{3+}	T_m (K)	E_a (eV)	s (s^{-1})	x	ℓ
Gd_2O_3: Eu^{3+}	2.5	390.2	0.44	8.70E+04	0.26	1.3
	3.0	390.2	0.51	7.60E+05	0.21	1.3
	2.0	390.2	0.51	8.90E+05	0.32	1.5
	1.5	390.2	0.46	1.90E+05	0.35	1.5
	1.0	390.2	0.44	1.10E+05	0.41	1.7

It has been observed by most of the workers engaged in same work [7-11] that glow curves do not change shape much with variation in concentration of activator or doping. The nature of glow peak approximately remains same for all the concentration. In some cases marginal shift in peak temperature has observed. The integrated area and intensity of the glow curve was observed to enhance with change in concentration of doping till certain limit of doping concentration and then decreases. Increase in intensity could be due to an enhancement in lattice defects i.e., trapping centers followed by trapping of more electrons/holes by defect centers. Decrease in T L intensity after certain concentration level is named as concentration quenching and could be due to the increase in dominance of non-radiative competent centers over recombination centers after this concentration of doped ions, resulting in a fall in the TL intensity. This may also be understand from destroy of luminescence centre after over concentration dose. Destroy of luminescence centre is due to step by step interaction between the luminescence centres by doping concentration. The probability of energy transfer is proportional to distance between luminescence centres. The distance between luminescence centres decreases with increasing doping concentration. After concentration quenching due to this decreased distance between luminescence centres the phenomenon of step by step energy transfer sharply enhanced, which results in the decrease of the TL intensity. Dexter theory of dipole–quadrupole (d–q) interaction is also helpful in understanding mechanism involved in concentration quenching [14].

Conclusion:

Decay parameters, order of kinetics along with extent of retrapping for $BaAl_2O_4$:Eu^{2+}, $BaMgP_2O_7$:Ce^{3+}:Tb^{3+}, $Mg_5(BO_3)_3F$:Dy^{3+} and Gd_2O_3: Eu^{3+} phosphor materials are evaluated from experimentally reported glow curves for different concentrations of doping material $Eu^{2+,}$ Ce^{3+}, Dy^{3+} and Eu^{3+} respectively. Prakash method of analysis is found to be simpler, convenient and free from any type of assumptions or limiting conditions. It has been found that order of kinetics and extent of retrapping are affected by changing concentration. Reason of concentration quenching regarding increase and decrease in intensity has also been discussed up to some

extent.The analysis helps in selecting good materials for persistent phosphors and also for dosimetric applications.

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