T L decay parameters and extent of retrapping from experimentally reported and numerically generated Thermoluminescence spectrum

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Abstract (10pt)

In present work we analyze the suitability and feasibility of analysis method, developed on mechanism proposed by Prakash, for the determination of T L decay parameters, namely the activation energy or trap depth, frequency factor and order of kinetics or extent of retrapping, of a thermoluminescence (TL) spectrum by applying it to both experimentally reported TL spectrums or glow curves of specimens Natural Biotite $[K(Mg,Fe)_3AlSi_3O_{10}(F,OH)_2]$, a mineral within the mica group, and Copper doped ZnS and to a TL glow curve of hypothetical system. It is found that the method is simpler, convenient and can be used for glow curves of any order of kinetics or any extent of retrapping.

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1. Introduction

In an insulator or a semiconductor, an excited electron in conduction band from valence band may either recombine quickly with an oppositely charged centre (results in fluorescence) or gets trapped at the trap centre. Once it is trapped at the trap centre it needs an external energy for exciting it again to the conduction band, because direct transition from trap centre to recombination centre is prohibited, wherefrom it may recombine with an oppositely charge centre present at the recombination centre emitting a photon (results in luminescence). If the external energy is supplied thermaly it is known as thermoluminescence (TL). The variation of TL intensity with temperature is known as TL spectrum or glow curve.

In an attempt to explain the TL glow curve, Adirovitch [1] proposed a set of three equations, which controls the traffic of electrons from trap centre to recombination centre via conduction band. These equations are considered as the basic equations which have been used by various workers to explain the occurrence of TL glow curve [2]. Mechanisms inherent in systems involving first order kinetics or monomolecular kinetics are supposed to be recombination dominant with negligible or zero retrapping [3]. It has been reported that probabilities of recombination and retrapping are equal in systems involving second order kinetics [4]. Further, a general equation for second and higher order equations has developed [5], whereas this general equation does not give the equation for first order kinetics. An expression for peak of a general order TL glow curve has been also developed [5], which decides the location of TL glow peak in the cases involving second and higher order kinetics including first order.

2. Mechanism involved in TL process

Ability of equation of general order TL glow peak to explain TL glow peak of any order of kinetics and inability of general equation of TL intensity to explain first order TL intensity led Prakash to reinvestigate into the mechanisms involved in thermoluminescence process. In view of these observations a model has been proposed by Prakash [6], by modifying Adirovitch set of equations. This model is found to

be able to explain the occurrence of TL glow curve involving second and higher order including first order kinetics successfully. The expression for TL glow curve intensity I, involving retrapping to the extent of x is given by [6]

$$I = (1 - x)\mathrm{n}_0 s \exp[- \frac{E_a}{k\,T} - \frac{s\,(1-x)}{b} \int_{T_o}^{T} \exp\left(- \frac{E_a}{k\,T'}\right) dT'] \qquad (1)$$

where n_o is the initial concentration of trapped electrons per unit volume at T_o, T_o is the initial temperature wherefrom TL glow curve starts to appear, s is the preexponential or escape frequency factor, E_a is the activation energy or trap depth, k is the Boltzman's constant, T is the absolute temperature, b is the constant linear heating rate and T' an arbitrary temperature in the range T_o to T.

Equation for TL peak is given by [6]

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

where τ_m is the relaxation time at peak temperature T_m and is given by Arrhenius relation [7] as

$$\tau_m = \tau_o \exp[\frac{E_a}{k\,T_m}] \qquad (3)$$

where τ_o is the fundamental relaxation time or relaxation time at infinite temperature and is related to escape frequency factor s through

$$\tau_o = \frac{1}{s} \qquad (4)$$

It has been widely reported in the literature [2, 8, 9, 10, &11] that b and n_o do not change the characteristic features E_a and s of the system. With changing b the rate of recombination changes resulting in the changed value of T_m. Also, E_a and s do not change with changing n_o, only the intensity of the corresponding TL glow curve changes provided the concentration is low.

Equation for initial concentration of trapped electron n_o is given by

$$n_o = \frac{1}{b} \int_{T_o}^{\infty} I(T') dT' = A_o \qquad (5)$$

where A_o is the total area enclosed by the TL glow curve. Concentration of electrons in trap centre at temperature T is given by

$$n = \frac{1}{b} \int_{T}^{\infty} I(T') dT' = A_T \qquad (6)$$

where A_T is the area of the TL glow curve in the temperature range T to ∞.

Before developing equations for the evaluation of TL decay parameters, mechanisms inherent in the TL decay process have to be taken into consideration. Retrapping of some of electrons after excitation decreases the number of electrons in the conduction band available for recombination. Consequently, the intensity of TL glow curve decreases. However, such decrease in the TL intensity does not change the characteristic features of the TL decay parameters i. e., E_a and s of the specimen. The intensity of TL glow curve at T_m and the area enclosed in the TL glow curve decrease due to less number of electrons available for recombination. This argument is supported through eq. (5). It would be worth mentioning just for the sake of reference that T_m is independent of n_o and appears at the same location if b is kept fixed [12]. TL and ionicthermocurrent (ITC) spectra recorded in these specimens shall give the same values of E_a and s as they belong to the same system because similar findings have been recorded in many TL glow curves and ITC spectra. No dependence of dielectric relaxation parameters on the concentration of impurity vacancy (IV) dipoles has been observed [12] provided the concentration is low and the relaxation is Debye type . In the initial rise method suggested by Bucci, Fieschi and Guidi [12], ln [I] plotted against (1 / T) in the same system results in a number of parallel straight lines corresponding to different concentrations of IV dipoles suggesting unchanged value of E_a. The intercept changes because of the change in number of IV dipoles keeping s unchanged. It is thus obvious that different TL glow curves recorded on the same specimen may have different values of x but TL decay parameters E_a and s shall come out to be the same. This conclusion about TL decay parameters has been derived from ITC measurements particularly because of the fact that ITC spectrum is very much similar to TL glow curve involving monomolecular or first order kinetics [12].

Based on the discussions of the preceding paragraph, it is obvious that the characteristic features of the TL decay parameters E_a and s of the system do not change due to different extents of retrapping. The evaluated values of E_a and s may 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 eq. (1) for $x = 0$ becomes

$$I = n\,s \exp[(- \frac{E_a}{k\,T})$$

which can be rearranged as

$$ln\left[\frac{n}{I}\right] = ln\left[\frac{1}{s}\right] + \frac{E_a}{k\,T} \qquad (7)$$

It is obvious that one gets a straight line when ln [n / I] is plotted against (1 / T) in accordance with eq. (7). The slope of the line gives the value of E_a and from the intercept one gets the value of s. Thus,

characteristic TL decay parameters E_a and s are evaluated. It would be worth reiterating that the characteristic TL decay parameters E_a and s of the system do not depend on the extent of retrapping. The value of x has been evaluated using eq. (2).

3. Analysis of TL spectrum

In above discussion it is clear that, in order to determine TL decay parameters and extent of retrapping of any TL spectrum using analysis method based on theory proposed by Prakash, one has to evaluate $(\frac{n}{I})$ which is given by the area of a TL spectrum from the temperature under consideration until the end point and corresponding intensity.

3.1. Analysis of experimentally reported TL spectrums

Following the analysis method suggested in pevious section, experimentally observed TL spectrums, already reported in literature, of specimens Natural Biotite (a mineral within the mica group)[13] and Copper doped ZnS[14] are analyzed and the results are given below

Table 1:Data from experimentally reported curve [13]

Specimen- Natural Biotite [$K(Mg,Fe)_3AlSi_3O_{10}(F,OH)_2$]					
T(K)	1/T	n(a.u.)	I(a.u.)	n/I	ln[n/I]
360	0.00277778	370	8	46.25	3.834061464
380	0.00263158	280	32	8.75	2.1690537
400	0.0025	72	37	1.945946	0.665748206

According to eq.(7) plot of ln[n/I] vs 1/T is shown in Fig.1. From experimentally reported curve, T_m = 393K, I_m = 47 a.u., b = 2 K/s, n_0 = 384.5 a.u.. Boltzman's constant k = 8.617E-5 eV/K.

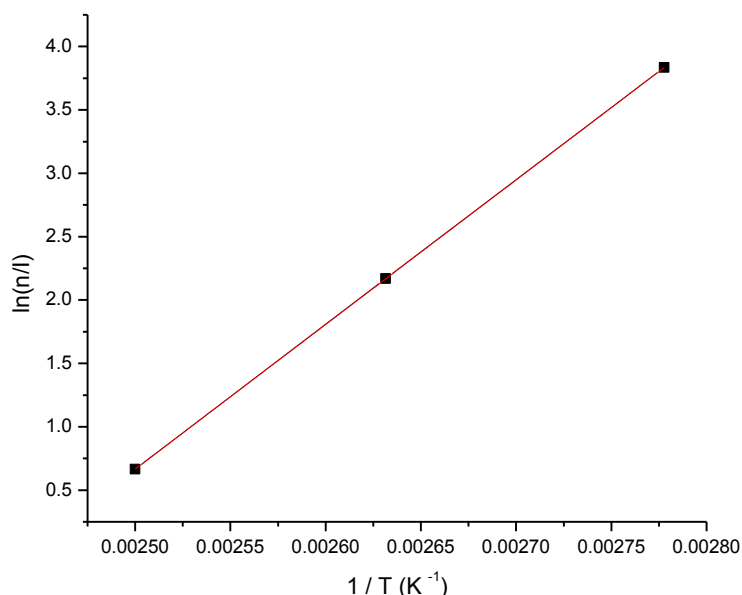**Fig. 1: Plot of ln [n/ I] versus [1 / T] for Specimen- Natural Biotite[13].**

From Fig.1 slope = 11405.609 and intercept = -27.8474. Using eq.(7),(2),(3) and (4) calculated values of different parameters are as given below
(i) Activation Energy E_a = 0.982821 eV ,
(ii) Escape frequency factor s = 1.24156E+12

(iii) Extent of retrapping $x = 0.52$.

Data corresponding to experimentally reported TL spectrum of specimen Copper doped ZnS are given in Table 2. According to eq.(7) plot of $ln[n/I]$ vs $1/T$ is shown in Fig.2. From experimentally reported curve, $T_m = 373K$, $I_m = 44$ a.u., $b = 1$ K/s, $n_0 = 411$ a.u.. Boltzman's constant $k = 8.617E-5$ eV/K.

Table.2 Data from experimentally reported curve [14]

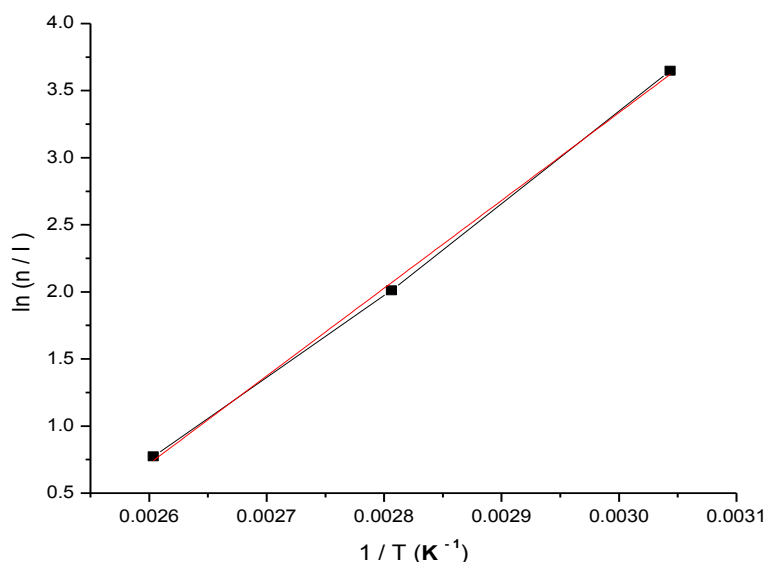| Specimen-Copper doped ZnS					
T(K)	1/T	n(a.u.)	I(a.u.)	n/I	ln[n/I]
328.5556	0.00304363	384	10	38.4	3.64805746
356.3333	0.00280636	269	36	7.472222	2.011192441
384.1111	0.00260341	65	30	2.166667	0.773189888

Fig. 1: Plot of ln [n/ I] versus [1 / T] for Specimen- Copper doped ZnS [14].

 From Fig.2 slope = 6540.93887 and intercept = -16.2869. Using eq eqs.(7),(2),(3) and (4) calculated values of different parameters are as given below
(i) Activation Energy $E_a = 0.563633$ eV ,
(ii) Escape frequency factor s = 11839003.26
(iii) Extent of retrapping $x = 0.84$.
TL spectrums for hypothetical system, with same values of E_a, s and n_o but different values of ℓ constructed with the help of eqs. (1) and

$$\ell = \frac{1}{(1-x)} \qquad\qquad (8)$$

where ℓ is known as order of kinetics. Constant linear heating rate b is same. TL spectrums are shown in Fig.3.
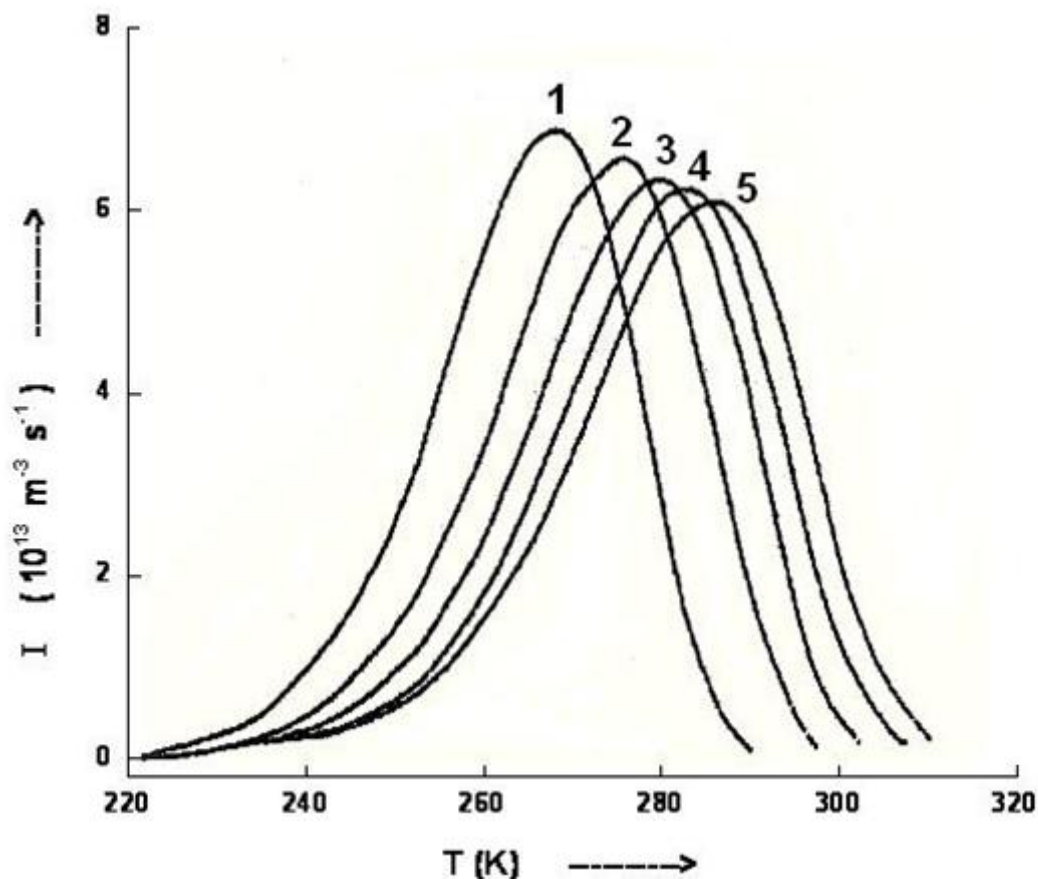
Fig.3: TL spectrums for hypothetical systems having same parameters $E_a = 0.55$ eV, $s = 2 \times 10^8$ s^{-1}, $n_o = 2 \times 10^{16}$ m^{-3} and $b = 0.1$ Ks^{-1} for different order of kinetics. The number on the curves indicates the involved order of kinetics.

For the evaluation of TL decay parameters, $\ln [n / I]$ for glow curves of Fig.3 are plotted against $[1 / T]$ in Fig. 4. It is obvious that one gets a straight line in accordance with eq. (7). The slope gives the value of E_a whereas the value of s is obtained from the intercept. x is evaluated with the help of eq. (2),(3) and(4) and corresponding value of ℓ is obtained using eq. (8).
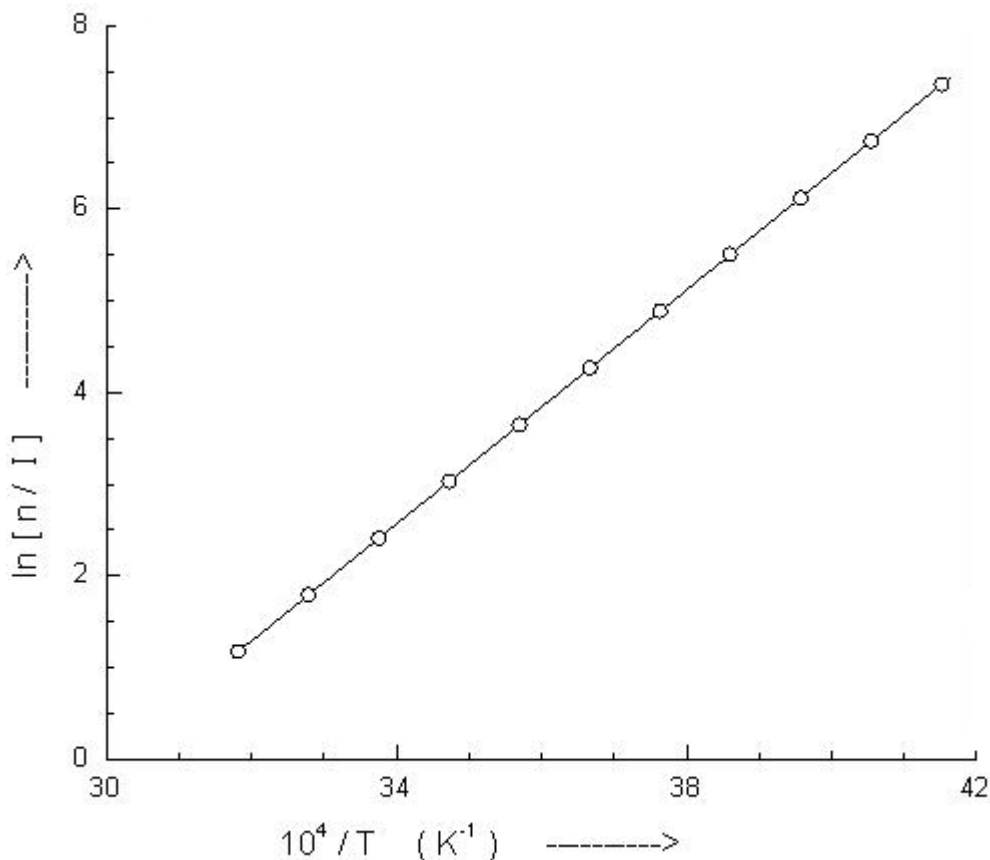
Fig.4: Plot of ln [n / I] versus [1 / T] for TL spectrums of figure 3.

The value of n_o is obtained using eq. (5). Evaluated values of E_a, s, x or ℓ and n_o corresponding to curves 1 to 5 of Fig. 3 are presented in Table 3.

<u>Table 3</u> **Evaluated values of TL decay parameters and order of kinetics for hypothetical system of figure 3.**

Curve No.	Evaluated with the help of eq.				
	(7)		(2)	(8)	(5)
	E_a (eV)	s x 10^{-8} (s^{-1})	x	ℓ	n_o x 10^{-16} (m^{-3})
1	0.55	2	0.10	1.11	2
2	0.55	2	0.49	1.96	2
3	0.55	2	0.67	3.03	2
4	0.55	2	0.75	4.00	2
5	0.55	2	0.81	5.26	2

4. Conclusion

In the present paper we have analyze experimentally reported TL spectrums of different specimen and numerically generated TL spectrum of hypothetical system, and evaluate all the three parameters E_a, s and x, following the Prakash method. This method for the evaluation of TL decay parameters E_a and s is in fact

BFG method [12] represented through eqs. (7). Consequently, the accuracies associated with the evaluation of E_a and s shall be the same as that obtained in BFG method. It is obvious that the Prakash method is simpler and convenient for the evaluation of dielectric relaxation parameters. No simplifying assumptions have been incorporated by Prakash in developing eq. (1). Activation energy and pre-exponential factor are characteristic features of the specimen and unaffected by the experimental conditions. The experimental conditions decide the extent of retrapping or order of kinetics involved. It is because of this reason that different TL runs recorded on the same specimen give different values of x or ℓ. Further, the dependence of peak temperature T_m on n_o is also excluded in the suggested model.

Acknowledgements

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