Ultra Scientist Vol. 24(3)B, 489-496 (2012).

T L Glow Curve Analysis Technique for Evaluation of Decay Parameters and Order of Kinetics

DEVENDRA PRASAD[1], A. N. THAKUR[2], and JAI PRAKASH[3]

(Acceptance Date 30th October, 2012)

Abstract

In the present paper a new method has been developed to evaluate decay parameters and order of kinetics by analyzing thermoluminescence (TL) glow curve. It has been observed that the decay parameters are characteristic feature of the system under investigation whereas order of kinetics does not. Extents of recombination and simultaneous retrapping decides the order of kinetics involved in the T L process. Order of kinetics increases with extent of retrapping within the system. TL decay parameters, order of kinetics and initial concentration of trapped electrons per unit volume are evaluated easily and conveniently following the proposed method of analysis.

Key words: Thermoluminescence, Decay parameters, Order of kinetics, Recombination and retrapping of electrons.

1. Introduction

Among the different techniques of thermally stimulated processes for investigation of trap levels in insulating solids, thermoluminescence (TL) is an important and convenient method. Thermoluminescence is a potentially powerful tool for the understanding of the mechanism of light emission during thermal stimulation and also for the determination of decay parameter (activation energy and escape frequency factor) and order of kinetics involved in the process. A plot of TL intensity (I) versus temperature (T) resulting due to uniform rate of heating the system under investigation is called TL glow curve. TL glow intensity with first order kinetics is expressed[1,2]

$$I_1 = n_o s_1 \exp[-E_a/(kT) - (s_1/b) \int_{To}^{T} \exp\{-E_a/(kT')\} dT'] \quad (1)$$

where n_o represents 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 Boltzman's constant, b the linear heating rate, T_o the temperature at which TL glow curve starts to appear, T' any arbitrary temperature in the range T_o to T. Suffix 1 represents the involvement of first order kinetics. It has been pointed out by Randall and Wilkins[2] that first order kinetics is recombination dominant process. In the situations when probabilities of recombination and retrapping are equal[3], one observes a TL spectrum with second order kinetics. Corresponding intensity of the TL glow curve is represented by

$$I_2 = n_o^2 s_2 \, [\exp\{-E_a/(kT)\}].[1+\{(n_o s_2)/b\} \int_{To}^{T} \exp\{-E_a/(kT')\}dT']^{-2} \quad (2)$$

The escape frequency factor s_2 for second order kinetics is a constant quantity with the dimension $m^3 s^{-1}$. Parameters s_1 and s_2 are related as

$$s_1 = N \, s_2 \quad (3)$$

where N is the concentration of total electron traps per unit volume. Further according to Chen and Winer[4], the intensities of second and higher order TL glow intensity are represented by

$$I_L = n_o^L s_L \, [\exp\{-E_a/(kT)\}].[1+ \{n_o^{(L-1)}. s_L. (L-1) / b \} \int_{To}^{T} \exp\{-E_a/(kT')\}dT']^{-\{L/(L-1)\}} \quad (4)$$

where L represents the order of kinetics involved. Eq.(4) changes to eq.(2) for L = 2. Parameters s_1 and s_L are related through

$$s_1 = N^{(L-1)} s_L \quad (5)$$

where s_L has the dimension $[m^{3(L-1)}.s^{-1}]$. Eq.(5) changes to eq.(3) for L = 2. In the cases when all the available electron traps are filled initially (*i.e.* when $N = n_o$) eq.(4) changes to

$$I_L = n_o \, s_1 \, [\exp\{-(E_a/(kT)\}].[1+\{s_1.(L-1)/b\} \int_{To}^{T} \exp\{-E_a/(kT')\}dT']^{-\{L/(L-1)\}} \quad (6)$$

It is obvious that the intensity of TL glow involving first order kinetics represented through eq. (1) can not be obtained from eq. (6), whereas the intensities of TL glow curves involving second and higher order kinetics can be obtained from eq. (6).

It has been reported by Chen and Winer[4] that the peak of a general order TL glow intensity involving L^{th} order of kinetics appears at T_{mL} controlled by

$$[1+\{s_1(L-1)/b\} \int_{To}^{TmL} \exp\{-E_a/(kT)\}] = [\{L \, s_1 k(T_{mL})^2\}/bE_a]\exp\{-E_a/(kT_{mL})\} \quad (7)$$

Eq (7) decides the location of TL glow peak in the cases involving second and higher order kinetics including first order.

Thus, the general expression [eq.(7)] for TL glow peak is true for all the values of L but the general expression for TL glow intensity [eq.(6)] does not true for all values of L. To remove anomaly associated with eqs. (6) and

(7) number of attempts have been made[5-13] by different workers for developing suitable mechanism responsible for the occurrence of TL glow intensity, but none of them has been found to be quite satisfactory.

2. *Theory:*

In view of observations discussed in previous section, a model has been proposed by Prakash[14] which is found to be able to explain the occurrence of TL glow intensity successfully and is free from anomalies discussed above. In his proposed model Adirovitch[15] set of equations are modified as

$$m = n \qquad (8)$$

$$-(dn/dt) = (1 - \boldsymbol{x})\, n\, s \exp[-E_a/(kT)] \qquad (9)$$

and

$$I = -(dm/dt) = (1-\boldsymbol{x})\, n\, s \exp[-E_a/(kT)] \qquad (10)$$

where m and n represents the densities of holes and electrons in the respective recombination and trap centres. In eq.(9) the term [n s exp(-E_a/kT)] on right hand side represents the electrons in conduction band after excitation and term [$\boldsymbol{x}$ n s exp{-E_a/(kT)}] represents part of excited electrons which are retrapped in trap centres i,e., $\boldsymbol{x}$ represents the fraction or part of excited electrons which are retrapped such that $0 \le \boldsymbol{x} \le 1$. Obviously, retrapping depends on $\boldsymbol{x}$. For $\boldsymbol{x} = 0$, retrapping is zero corresponding to first order kinetics and $\boldsymbol{x}$ = 0.5, retrapping 50% corresponding to second order kinetics and so on. Remaining electrons in the conduction band represented by right hand side of eq.(9) recombine with oppositely charge centres present at the recombination centre. Thus the rate of recombination and hence intensity of TL glow will be represented by eq.(10). As a result of recombination, m decreases and hence there is a negative sign in eq.(10). It is obvious that for $\boldsymbol{x} = 0$, it is 100% recombination whereas for $\boldsymbol{x} = 0.5$ the recombination probability is 50% and so on. With the help of eqs.(9) and (10), it can be shown just for the sake of justification that excited electrons become equal to the sum of retrapped and recombine electrons as excepted. Thus once the extent of retrapping is determined, the extent of simultaneous recombination shall automatically be decided.

From eq.(8), we have

$$(dm/dt) = (dn/dt) \qquad (11)$$

It is obvious that the relationship suggested by eq.(11) is also derived from eqs.(9) and (10) which justifies the validity of the ideas suggested by Prakash[14]. Further it will be justified to mention that it is not necessary to assume either $N = n_o$ [4] or $n_c << n$ for developing[1-15] the basic equations, where n_c is the density of electrons in the conduction band. Eq.(10) for I can be used to develop a general expression for TL glow curve involving any extent of retrapping. The general equation for the intensity of TL glow curve involving retrapping to the extent of $\boldsymbol{x}$ as developed by Prakash[14] is

$$I = (1-\boldsymbol{x})\, n_o\, s \exp[-\{E_a/(kT)\} - \{s(1-\boldsymbol{x})/b\} \int_{To}^{T} \exp\{-E_a/(kT')\}dT'] \qquad (12)$$

And equation for TL peak is

$$T_m^{\,2} = \{b\, E_a\, \tau_m/(1-\boldsymbol{x})\, k\} \qquad (13)$$

where τ_m is the relaxation time at TL glow intensity peak temperature T_m, whereas relaxation time at any temperature is given by Arrhenius

relation[16]. Eq. (13) gives the location of TL peak in the system involving retrapping to the extent of ***x.***

Expression for T_m corresponding to different values of ***x*** can be obtained from the eqn. (13). For first order kinetics (for zero retrapping) eq. (13) with ***x*** = 0 results into

$$T_m^2 = \{ (b E_a \tau_m) / k\} \qquad (14)$$

Eq. (14) for first order kinetics is also obtained from eq. (7) after substituting corresponding value of L.

3. *Method of Analysis:*

Eq.(10) with help of eq.(11) gives

$$\int_{no}^{o} dn = - \int_{o}^{\infty} I dT \qquad (15)$$

The system is heated following a linear heating rate b according to the relation

$$T = T_o + b\,t \qquad (16)$$

Eq. (15) gives

$$n_o = \frac{1}{b} \int_{To}^{\infty} I(T')dT' = A_o \qquad (17)$$

where A_o is the total area enclosed within the TL glow curve. Also eq.(15) in the limits t to ∞ can be written as

$$\int_{n}^{o} dn = - \int_{t}^{\infty} I dt \qquad (18)$$

This equation with the help of eq.(16) gives

$$n = \frac{1}{b} \int_{T}^{\infty} I(T')dT' = A_T \qquad (19)$$

where A_T is the area of the TL glow curve in the temperature range T to ∞. Activation energy and escape frequency factor (TL decay parameters) are the characteristic features of the system under investigation and 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 putting ***x*** = 0 in equation (10) which becomes

$$I = n\, s \exp(- E_a / kT)$$

This relation can be rearranged as

$$\ln [\, n/I \,] = \ln [1/s] + (E_a/kT) \qquad (20)$$

From eq. (20) one gets a straight line when ln [n/I] is plotted against (1/T). E_a can be evaluated from slope of the line and intercept gives the value of s. So in this way characteristic TL decay parameters 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. A justification to our proposal can be established after substituting the evaluated values of E_a and s into eq. (14) and observing that it is satisfied or not. It is noticed, however, that eq. (14) is not satisfied. Consequently, the value of ***x*** has been evaluated using eq. (13). Number of workers engaged in TL studies has used eq. (20) for the evaluation of TL decay parameters

without caring whether eq. (14) is satisfied or not. Thus value of E_a, s and $\boldsymbol{x}$ can be evaluated using eqs. (20) and (13).

Bucci, Fieschi and Guidi[16] have mentioned that the variation of current in the ITC (ionic thermocurrent) spectrum is very much similar to the intensity of a TL glow curve involving first order kinetics. Depolarization current I in an ITC spectrum involving L^{th} order of kinetics is given[18]

$$I = \{Q_o/(L\,\tau_o)\}\exp[\{-E_a/(kT)\} - \{1/(bL\tau_o)\} \int_{To}^{T} \exp\{-E_a/(kT')dT'] \quad (21)$$

Where Q_o is the total chrage released during ITC run and τ_o is the fundamental relaxation time. After comparing eqs. (12) and (21) for I, one finds a relationship between extent of retrapping $\boldsymbol{x}$ and order of kinetics involved L as

$$L = 1/(1-\boldsymbol{x}) \quad (22)$$

Eq. (22) tells that retrapping to the extent of $\boldsymbol{x}$ in TL process is equivalent to involvement of L^{th} order of kinetics in the dipoler reorientation process. n_o is evaluated using eq.(17) from total area enclosed within the TL glow curve.

Thus, TL glow curve can be analysed to evaluate the values of TL decay parameters E_a, s, $\boldsymbol{x}$ or L and n_o conveniently and easily using eqs. (20), (22) and (17) by suggested method of analysis.

4. Results and Discussion

In the mechanism of TL decay process, 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 this decrease does not changes the characteristic features of the TL decay parameters E_a and s of the specimen. The intensity of TL glow curve at T_m and the area enclosed in the TL curve decreases due to less number of electrons available for recombination. This argument is supported through eq. (17). 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[17]. A decrease in n_c due to retrapping suggests that n_c would have been more had there been no retrapping. Thus, decreased value of n_c means that a specimen of the same system with lesser concentration has been considered.

Consequently, decreased n_c due to different extents of retrapping may be regarded as to be due to different specimens with varying n_o of the same system. Obviously, TL and ITC spectra recorded in these specimens shall give the same values of E_a and s as they belong to the same system. Similar findings have been recorded in many TL glow curves and ITC spectra. In the initial rise method suggested by Bucci, Fieschi and Guidi[17], ln [I] plotted against (1 / T) in the same system results in a number of parallel straight lines corresponding to different concentration of IV dipoles as shown in Fig. 1, suggesting unchanged value of E_a. The intercept changes because of the change in number of IV dipoles keeping s unchanged.

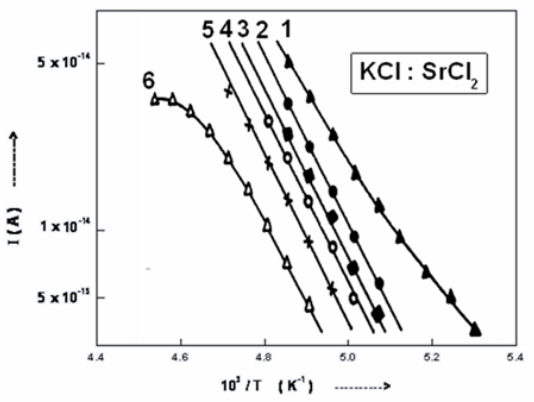

Fig. 1. Curve showing variation of ln[I] versus [1 / T] for six successive discharges recorded in KCl:Sr^{2+}single crystals [17].

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.

Eq. (12) with the help of eq. (22) can be rearranged in terms of L as

$$I = (1 / L)\, n_o\, s \exp\left[-(E_a / kT) - (s / L\, b) \int_{T_o}^{T} \exp(-E_a / kT')\, dT'\right] \qquad (23)$$

TL glow curves for hypothetical systems, with same values of E_a, s and n_o but differing values of L constructed with the help of eq. (23) following same value of constant linear heating rate b are shown in Fig. 2.

It is obvious that T_m shifts towards higher temperature with increasing value of L. Also, the intensity I_m of TL peak at T_m decreases with increasing value of L. For the evaluation of TL decay parameters, ln (n / I) of glow curves of Fig. 2 are plotted against (1 / T) in Fig. 3

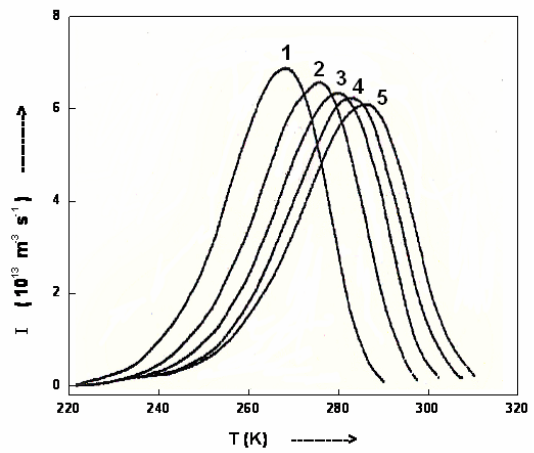

Fig. 2. Hypothetical systems TL glow curve (E_a= 0.55 eV,s = $2x10^8 s^{-1}$,and b=$0.1Ks^{-1}$, n_o =$2x10^{16}m^{-3}$ and b = $0.1Ks^{-1}$) having same parameters for different order of kinetics (shown on the top of the (curve).

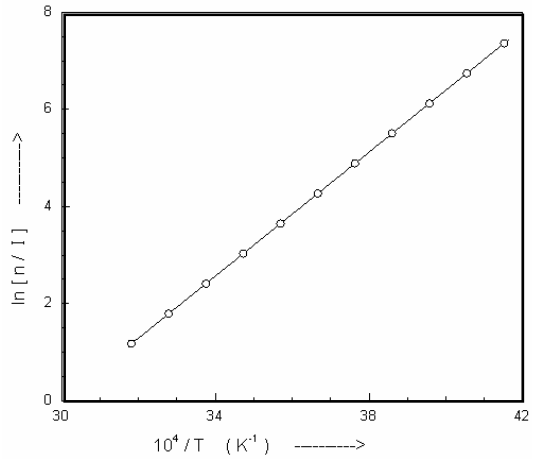

Fig. 3. Plot showing variation of ln[n/I] with [1/T] for different glow curves of figure 2.

It is obvious that one gets a straight line in accordance with eq. (20). 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. (13) and corresponding value

Table 1. Evaluated values of TL decay parameters and order of kinetics for hypothetical systems of figure 2

Curve No.	Evaluated with the help of eq.				
	(32)		(26)	(35)	(29)
	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

of L is obtained either using eq. (22). The value of n_o is obtained using eq. (17). Only one straight line in ln (n / I) versus (1 / T) in Fig. 3 is obtained because E_a, s and n_o are the same for all the glow curves of Fig. 2. Evaluated values of E_a, s, ***x*** or L and n_o corresponding to curves 1 to 5 of Fig. 2 are presented in table 1.

It is obvious that the evaluated values are in good agreement with the chosen values of the hypothetical systems. Thus, TL decay parameters are evaluated conveniently and easily following the suggested model. It would be worth mentioning that for L=1 of the hypothetical system of Fig. 2, retrapping to the extent of 10% is observed and the corresponding value of L is found to be 1.11. This suggests an inaccuracy of ±10% in the extents of retrapping and simultaneous recombination, and ±0.1 in the order of kinetics, respectively.

5. Conclusion

Out of the electrons excited to the conduction band, some are retrapped and balance get recombined in such a way that the sum of retrapped and recombined electrons is equal to the electrons excited to the conduction band. Based on the assumption free generalized theory as proposed by Prakash[14], for any extent of retrapping, a method has been developed to analyse TL glow curve for evaluation TL decay parameters, activation energy E_a and escape frequency factor or pre exponential factor s alongwith extent of retrapping ***x*** or order kinetics L and also initial concentration of trapped carriers per unit volume n_o. Intensity of TL peak is found to depend on the initial concentration of trapped electrons as awaited. Thus, TL decay parameters E_a and s alongwith ***x*** or L and n_o are evaluated conveniently and easily following the suggested method of analysis.

Acknowledgements

The first author is greatful to Director, U.P. Textile Technology Institute, Kanpur (U.P.), Principal, T.D. College, Jaunpur and H.O.D. Deptt. of Physics, T.D. College, Jaunpur for providing necessary facilities.

References

1. R. Chen and Y. Kirsh, 'Analysis of Thermally Stimulated Processes', Pergamon Press, Oxford, England 1981).
2. J.T. Randall and M.H.F. Wilkins, *Proc. Roy. Soc. A184*, 366 (1945).
3. G.F.J. Garlick and A.F. Gibson, *Proc. Roy. Soc. 60*, 574 (1948).
4. R. Chen and S.A.A. Winer, *J. Appl. Phys. 41*, 5277 (1970).
5. P.S. Majumdar, S.J. Singh and R.K.Gartia, J. Phys. D:Appl. Phys. *21*, 815 (1988).
6. Y. Kirsh, Phys. Stat. Sol. *a129*, 15 (1992).
7. J. Prakash, Solid State Commun. *85*, 647 (1993).
8. J. Prakash and D. Prasad, Phys. Stat. Sol. *a142*, 281 (1994).
9. P.K. Singh, Ph.D. Thesis, DDU Gorakhpur University, Gorakhpur (2002).
10. J. Prakash, S.K. Rai, P.K. Singh and H.O. Gupta, *Indian J. Pure Appl. Phys. 42*, 565 (2004).
11. J. Prakash, P.K. Singh and D.K. Dwivedi, *Indian J. Pure Appl. Phys. 44*, 532 (2006).
12. A. Katiyar and D. Prasad, *Dayanand J., Sci., 1*, 85 (2008).
13. Thermoluminescence Glow Curve Involving any Extent of Retrapping or Order of Kinetics: J. Praksh, Communicated to Pramana- Journal of physics.
14. E.I. Adirovitch, *J. Phys. Rad. 17*, 705 (1956).
15. S. J. Arrhenius, Phys. Chem. 226 (1889).
16. C. Bucci, R. Fieschi and G. Guidi, Phys. Rev. *148*, 816 (1966). A Model for the Occurrence and Analysis of Ionic Thermocurrent Spectrum Involving Different Order of kinetics: J. Prakash, accepted for publication in *Pramana-Journal of physics*.