



Thermally Stimulated Processes - II On The Appearance Of A Thermoluminescence Glow Curve

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Abstract: A model has been proposed which explains the mechanisms responsible for the appearance of a thermoluminescence (TL) glow curve. Adirovitch set of equations has been modified suitably. A generalized equation has been developed which is found to be capable of explaining TL intensities of different order of kinetics including first order. Methodology for the evaluation of TL decay parameter has also been developed. Form factor depending on the slope of the TL glow curve has been found to be helpful in assessing the order of kinetics involved.

Key Words: Thermoluminescence, glow curves, electron trap, Thermally Stimulated Process, Order .

1. Introduction:

When a substance is irradiated, electrons are raised to conduction band. In its return to valence band some electrons are trap to certain defect location or trap centres where they stay for longer time. These trapped electrons are release from their respective trap centre when the system is heated. Such released electrons may quickly recombine with an oppositely charged centres resulting in the appearance of a TL glow curve. Let us suppose that m and n represent density of holes and electrons in the recombination and trap centers at the time t , respectively. Recombination is the process through which m decreases. Thus the TL intensity, will be given by

$$i = (- dm / dt) = m n_c A_m \quad (1)$$

where n_c is density of electrons in the conduction band and A_m the recombination probability. Rate of decrease of n i.e. $(-dn/dt)$ will depend on the excitation of electrons into the conduction band and also on their retrapping. Thus

$$(- dn / dt) = n s_1 \exp(- E_a / kT) - (N - n) n_c A_n \quad (2)$$

Where suffix 1 represent the parameters associated with the first order kinetics. The first term on the right hand side of Eq.(2) represents obviously the rate of release of electrons from their respective traps and the second term represents the rate of retrapping. Apart from Eqs.(1) and (2), charge neutrality requires

$$m = n + n_c \quad (3)$$

Eqs. (1), (2) and (3) are known as Adirovitch set of equations describing the mechanisms responsible for the appearance of a TL glow curve.

Randall and Wilkins proposed that first order kinetics is a case of recombination dominant process with negligible retrapping. This condition in conjugation with Eqs.(1) and (3) results in the expression for the intensity of TL glow curve is

$$i_1 = n_0 s_1 \exp[(- E_a / kT) - (s_1/b) \int \exp(- E_a / kT') dT'] \quad (4)$$



where n_0 is initial concentration of trapped electron per unit volume, k the Boltzmann constant, T_0 absolute temperature wherefrom TL glows curve starts to appear and T' is an arbitrary temperature in the range T_0 to T .

Garlick and Gibson proposed that second order kinetics is a case of strong retrapping probability. When the experimental run is recorded following a constant linear heating rate b and the rate of retrapping and recombination are 50% each, the intensity of second order TL glow curve is given by

$$i_2 = n_0^2 s_2 \exp(-E_a/kT) \left[1 + (n_0 s_2/b) \int_{T_0}^T \exp(-E_a/kT') dT' \right]^{-2} \quad (5)$$

where suffix 2 represents the parameter associated with second order kinetics. Pre-exponential factor s_2 and s_1 are related through

$$s_1 = n_0 s_2 \quad (6)$$

For a general order TL glow curve it has been shown by Chen that the intensity of TL glow curve (when all the electron trap are filled initially i.e. $N = n_0$) is represented such that by

$$i_l = n_0 s_l n_0^{(l-1)} \exp[-E_{al}/kT] \left[1 + \{s_l n_0^{(l-1)}/b\} \int_{T_0}^T \exp(-E_{al}/kT') dT' \right]^{-(l-1)/(l-1)} \quad (7)$$

where suffix l represent the parameters associated with the l th order kinetics. Pre-exponential factor s_1 and s_l are related as

$$s_1 = s_l n_0^{(l-1)} \quad (8)$$

where s_l has the dimension $m^{-3(l-1)} s^{-1}$. It is obvious that Eq.(8) changes to Eq.(6) for $l = 2$.

It has been reported by Chen and Winer that the peak of a general order TL glow curve appears at T_M such that

$$\left[1 + \{s_l n_0^{(l-1)}/b\} \int_{T_0}^T \exp(-E_{al}/kT') dT' \right] = (l s_l n_0^{(l-1)} k T_M^2 / b E_{al}) \exp(-E_{al}/k T_M) \quad (9)$$

Eq.(9) decides the location of TL glow peaks in the cases involving second and higher order kinetics including that of the first order. It is apparent that the location of T_M is independent of n_0 in the first order kinetics as expected. However T_M is found to be dependent of n_0 in system involving second and higher order kinetics.



Failure of Eq.(7) to represent the intensity of first order TL glow curve and ability of Eqn.(9) to represent the position of the peak of general order TL glow curve led us to reinvestigate the mechanisms inherent in the TL processes. Further, the dependence of T_M on n_0 in systems involving second and higher order kinetics seems to be unrealistic. These anomalies have been resolved by Prakash by suggesting a modified form of Eq.(7). Later on it has been found that the modification proposed by Prakash has some inherent demerits. Consequently modified Adirovitch set of equation has been developed. As these modification explain the intensity of TL glow curve to a larger extent but have been found to be inadequate when different order of kinetics have been taken into consideration. Therefore mechanism responsible for the appearance of a TL glow curve is reconsidered in this article with an aim to establish a generalized equation.

(2). Suggested Mechanisms of Thermoluminescence:

The intensity of TL glow curve depends on the rate of recombination. It has been reported that first order kinetics is a recombination dominant process with almost zero or negligible retrapping where as rates of recombination and retrapping are equal for the process involving second order kinetics. Obviously, rate of recombination and retrapping should therefore depend on the order of kinetics involved. Consequently, Eq.(1) of Adirovitch set of equations should be represented as

$$I = - (d_m / dt) = (1/ l) m n_c A_m \quad (10)$$

It is obvious from Eq.(10) that the rate of recombination decreases with the increasing order of kinetics.

While deriving expression for TL intensity, it is assumed that first order kinetics is a recombination dominant processes i.e. $(n_0 - n) A_n = 0$. It can be possible when either $A_n = 0$ or $(n_0 - n) = 0$. The first term A_n cannot be zero and the second term $n_0 = n$ can only be possible just at the start of the experiment when all the available electron traps are filled initially. As soon as an electron is released from the trap, $(n_0 - n)$ will have some finite value and hence $(n_0 - n)$ cannot be equal to zero during an experimental run. Hence, $(n_0 - n) A_n$ can be set equal to zero for first order kinetics by expressing it as $((l - 1)/ l) (n_0 - n) A_n$. In view of this Eq.(2) of Adirovitch set of equations should be expressed as

$$-(dn / dt) = n s \exp(-E_a / kT) - ((l - 1)/ l) (n_0 - n) n_c A_n \quad (11)$$

It is obvious from Eq.(11) that the rate of retrapping increases with the increasing order of kinetics as wanted giving zero retrapping in system involving first order kinetics.

The neighborhood and environment, the trap and recombination centers of the system and the probabilities of recombination and retrapping will essentially decide the order of kinetics involved. Thus, in view of this, the charge neutrality requirement is expressed as

$$l m = n + n_c \quad (12)$$

Eqs.(10) to (12) are known as modified Adirovitch set of equations describing the mechanisms responsible for the appearance of a TL glow curve. These equations can be rearranged to give

$$I = (1/ l) n s \exp(-E_a / kT) [l m A_m / (l m A_m + (l - 1)(N - n)A_n)] \quad (13)$$

Eq.(13) give us the information about TL intensities of system involving different order of kinetics..



3. Expression for the intensity of a general order TL glow curve:

It is known facts that the first order kinetics is recombination dominant process whereas rate of recombination and retrapping are equal in second order kinetics. For a TL glow curve involving l th order of kinetics rate of recombination and retrapping are related as

$$(l-1) (1/l) m n_c A_m = ((l-1)/l)(n_0-n) n_c A_n \quad (14)$$

Obviously for l th order of kinetics, $(l-1) \times$ rate of recombination = rate of retrapping. In Eq.(14), $(1/l)mn_cA_m$ represents the rate of recombination whereas $((l-1)/l)(n_0-n)n_cA_n$ represents the rate of retrapping. Eq. (13), in the light of Eq. (14) results into

$$I = \{1/(2l-1)\} (n / \tau) \quad (15)$$

where τ is the mean life time or the relaxation time at the temperature T expressed as.....

$$\tau = (1/s) \exp [E_a/kT] \quad (16)$$

Eq.(15) can be solved to give

$$n = n_0 \exp [(-l / (2l-1)) (t/ \tau)] \quad (17)$$

Non-isothermal form of Eq.(17) can be written

$$n = n_0 \exp [(-l / (2l-1)) \int_0^t (dt / \tau)] \quad (18)$$

Combination of Eqs.(25) and (28) gives

$$i = [1/(2l-1)](n_0/\tau) \exp [(-l / (2l-1)) \int_0^t (dt / \tau)] \quad (19)$$

If the system is heated following a constant linear heating rate b one gets from Eq. (19)

$$i = [1/(2l-1)]n_0s \exp\{(-E_a/kT) - \{ls/b(2l-1)\} \int_{T_0}^T (\exp (-E_a / kT')dT')\} \quad (20)$$

Eq.(20) is the generalized equation for expressing the intensity of general order TL glow curve. Expressions for the TL intensity of different order of kinetics can be obtained from Eq.(20) after substituting the corresponding values of l as 1, 2, 3, 4 ...etc. It is obvious that Eq.(20) results into Eq.(4) for $l = 1$. Thus Eq.(20) is entitled to be named as a generalized equation for expressing the intensity of a general order TL glow curve. TL glow curves involving different order of kinetics in a hypothetical system obtained following Eq.(20) are presented in Fig 1. It is obvious from figure that I_M decreases with increasing order of kinetics for the same value of n_0 . The extent of decrease is more one passes from $l = 1$ to $l = 2$. It is also observed that T_M shifts towards higher temperature when involved order of kinetics increases



4. Evaluation of TL decays parameters:

From Eq.(13), one gets

$$I = (-1/t) dn/dt \quad (21)$$

If the system is heated following a constant linear heating rate b , Eq.(21) after integration yields into

$$n = (t/b) \int_T^{\infty} I(T')dT' = \nu A_T \quad (22)$$

And

$$n_0 = (t/b) \int_{T_0}^{\infty} I(T')dT' = \nu A_0 \quad (23)$$

It is worth mentioning just for the sake of continuity that n is the number of trapped carrier per unit volume at the temperature T corresponding to time t and A_T represents the area of the TL glow curve enclosed within the temperature range T to ∞ such that

$$A_T = (t/b) \int_T^{\infty} I(T')dT' \quad (24)$$

And A_0 represents the total area enclosed within the TL glow curve such that

$$A_0 = (t/b) \int_{T_0}^{\infty} I(T')dT' \quad (25)$$

Rearrangement of Eqs.(15) and (22) gives

$$\ln(X_T) = \ln\{(2t-1)/ts\} + E_a/kT \quad (26)$$

Where

$$X_T = (A_T/I) \quad (27)$$

For a given TL glow curve, decay parameters ν , s and E_a are constant, so the plot of $\ln(X_T)$ versus $(1/T)$ will be a straight line with the slope (E_a/k) and intercept equal to $\ln\{(2t-1)/ts\}$. Such straight line plots in $\ln(X_T)$ versus $(1/T)$ are shown in Fig.2. Thus, the activation energy can be evaluated from the slope of the straight line plot. The intercept gives the value of either ν or s provided the other is known. It is required therefore to establish a methodology for the evaluation of ν or s .

As far as order of kinetics is concerned various attempt has been made for its evaluation by different workers. With an aim to evaluate the order of kinetics May and Patridge have suggested a method which utilize the data of isothermal TL decay curves. These data have also been used by Haris and Jackson for suggesting a procedure for the evaluation of the order of kinetics. These methods are, however, not suited to be used for the analysis of TL glow curve. Chen has suggested a symmetry parameter $\mu_g = (T_2 - T_M)/(T_2 - T_1)$ depending of the shape of TL glow curve, which helps in the evaluation of ν . For first order glow curve μ_g is found to be 0.42 where as for a TL glow curve involving second order kinetics it is found to be 0.52. It has been observed by Chen et.al that the peak of a second order TL glow curve shifted towards lower temperature with increasing value of initial trap filling. Consequently, they have suggested a method, in which different peaks are shifted in such a way that they are located at the same temperature. Such a shifting in peak result in the value of ν . Gartia, Singh and Mazumdar have shown that μ_g happens to be a function of the fractional intensity of the TL glow curve. They have suggested a method for the evaluation of ν using $\mu_g(x)$ in place of μ_g where x represent the fractional intensity of TL glow curve. These above mentioned procedures have been applied by us to establish a criterion for ascertaining the value of ν . It has been observed that none of them is suitable for the evaluation of ν . To establish a deciding parameter which helps in the evaluation of ν we have tried and calculated the values of $\{T_M/(T_2 - T_1)\}$, $\{(T_M - T_1)/(T_2 - T_1)\}$, $\{(T_M - T_1)/(T_2 - T_M)\}$ etc. but none of them found to be conclusive. The value of $\{T_M/(T_2 - T_M)\}$ named as form factor γ , only gives satisfactory result for the evaluation of the order of kinetics. The calculated value of form factor of different values of E_a , s and ν are shown in table-1. From this table it is clear that the average value of form factor for first order kinetics is



24.15, for second order kinetics it is 23.27 and for third order kinetics it is 22.33 and so on. A graph plotted between the average values of form factor γ versus order of kinetics ι is shown in Fig.3. It is clear that for a known value of form factor, the order of kinetics involved in the system can be ascertained from the theoretical curve. Once the order of kinetics is known, the pre-exponential factor can be evaluated from the intercept of the straight line plot drawn in accordance with Eq.(26). Thus the TL decay parameters E_a , s and ι can be evaluated.

5. Discussion:

In the proposed model, all the anomalies mentioned in section 1 are removed. The location of the peak of general order TL glow curve can be ascertained with the help of Eqn.(20). It is found that T_M depends on b , ι , E_a and s through relation

$$T_M^2 = ((2\iota - 1) / \iota) [b E_a \tau_M / k] \quad (28)$$

where T_M is the temperature at which maximum intensity I_M of the TL glow curve appears and τ_M is the corresponding relaxation time at T_M . It is obvious that T_M is independent of n_0 as expected. The earlier finding that T_M is a function of n_0 for second and higher order kinetics is also remedied through the suggested model. Further s of different order kinetics is found to be independent of each other as expected. Also the unit of pre-exponential factor is found to be s^{-1} as per the requirement of the Arrhenius relation, whereas in the previous relation the unit of pre-exponential factor is $m^{3(\iota - 1)}s^{-1}$, which is in contradiction to the Arrhenius relation. A system will obviously involve a particular order of kinetics and correspondingly it will have its own TL decay parameters ι , E_a and s . Thus the value of s in different order of kinetics other than the one involved in the system under investigation has no meaning and their interrelationship is not justified. It is thus obvious that the shortcomings of the earlier suggested model are removed through the proposed model. Thus Eq.(20) seems to be the right expression to represent the intensity of a general order TL glow curve.

Figure Captions:

Fig. 1. TL glow curves of different order of kinetics in a hypothetical system with $E_a = 0.50$ eV., $s = 2 \times 10^8$ s⁻¹, $b = 0.1$ Ks⁻¹ and $n_0 = 2 \times 10^{16}$ m⁻³. Values of E_a and s are assumed to be the same in different order of kinetics. The number on curves indicates the involved order of kinetics.

Fig.2. Plot of $\ln [X_T]$ vs $[1 / T]$ for different order of kinetics in a hypothetical system with $E_a = 0.50$ eV., $s = 2 \times 10^8$ s⁻¹, $b = 0.1$ Ks⁻¹ and $n_0 = 2 \times 10^{16}$ m⁻³. The number on curves indicates the involved order of kinetics.

Fig.3. Plot of average value of form factor vs order of kinetics for a TL glow in curve.

Table – 1

Form factor of TL glow curves for different sets of E_a , s and τ

E_a (eV.)	s (s^{-1})	Form Factor $\gamma = [T_m / (T_2 - T_m)]$		
		$\tau = 1$	$\tau = 2$	$\tau = 3$
0.50	1.0×10^8	24.10	23.18	22.26
0.50	1.5×10^8	24.30	23.22	22.22
0.50	2.0×10^8	24.33	23.27	22.53
0.50	2.5×10^8	24.00	23.31	22.43
0.50	3.0×10^8	24.10	23.23	22.27
0.50	3.5×10^8	24.15	23.28	22.34
0.50	3.5×10^8	24.18	23.25	22.24
0.55	1.0×10^8	24.12	23.38	22.51
0.55	1.0×10^8	24.20	23.20	22.28
0.55	1.5×10^8	24.10	23.46	22.23
0.55	2.0×10^8	24.25	23.35	22.52
0.55	2.5×10^8	24.55	23.28	22.46
0.55	3.0×10^8	24.00	23.26	22.19
0.55	3.5×10^8	24.02	23.31	22.26
0.60	1.0×10^8	24.01	23.33	22.48
0.60	1.5×10^8	24.14	23.29	22.29
0.60	2.0×10^8	24.10	23.10	22.10
0.60	2.5×10^8	24.16	23.31	22.30
0.60	3.0×10^8	24.00	23.30	22.41
0.60	3.5×10^8	24.15	23.21	22.39
0.60	3.5×10^8	24.15	23.25	22.29
Average value of form factor γ		24.15	23.27	22.33

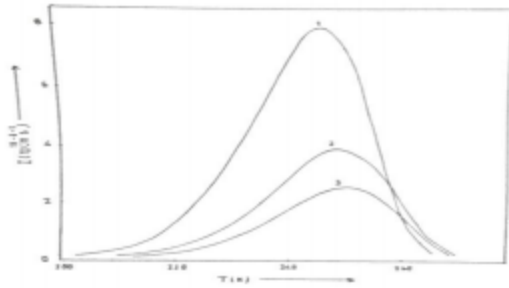


FIG. 1

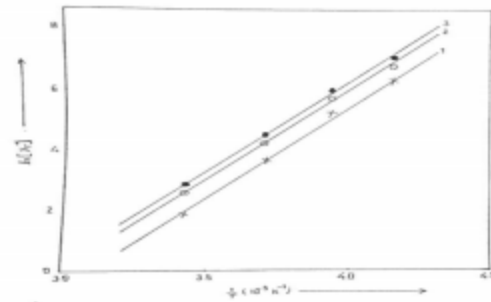


FIG. 2

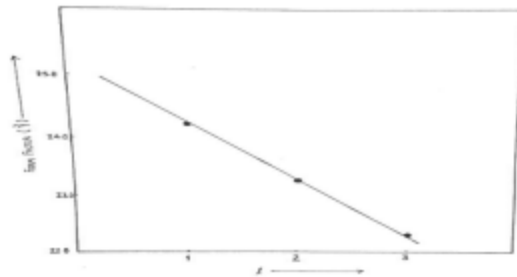


FIG. 3



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