



On the analysis of thermoluminescence peaks in light of various models

MAHUA KARMAKAR^{a,*}, P.S.MAJUMDAR^a AND S.D. SINGH^b

^aDepartment of Physics, Acharya Prafulla Chandra College,
New Barrackpore, Kolkata, West Bengal- 700 131, India

^bDepartment of Physics, Manipur University, Canchipur,
Imphal, Manipur-795 003, India

*Corresponding author: e-mail mahua_apc@yahoo.com

Abstract

Thermally stimulated luminescence, popularly known as thermoluminescence (TL) arises from the excitation of an insulator or semiconductor usually by ionizing radiation followed by a read out stage of heating the sample and measuring the light emitted, in excess of black body radiation. The understanding of the phenomenon is connected with the energy band theory of solids and has to do with the trapping of charge carriers in the forbidden energy gap called traps associated with imperfections in the crystalline materials, usually the defects. The rigorous theory of TL involves the solution of a set of coupled differential equations describing the trafficking of charge carriers between valence band, conduction band and traps. Activation energy and the order of kinetics are two important trapping parameters associated with TL. In the present paper, we consider the suitability of modified peak shape (MPS) and Kirsh method of determination of these two parameters in light of three models namely (1) General order kinetics (GOK) model, (2) One trap one recombination centre (OTOR) model and (3) Interacting multitraps system (IMTS) model

Finally, the applicability of our theoretical analysis has been supplemented by analyzing experimental TL peaks of β -irradiated quartz.

Keywords: Thermoluminescence; Activation energy, Order of kinetics; Peak shape method, Kirsh method

1. Introduction

Thermally stimulated luminescence (TSL) commonly known as Thermoluminescence (TL) has found important applications in dating and dosimetry [1, 2]. In these applications, stability of TL peak is crucial since the life-time of a TL peak and thus the time range over which it might be important for dating and dosimetry depends upon the trapping or kinetic parameters namely activation energy, the order of kinetics and the frequency factor. In the literature, a large number of methods are available for the determination of activation energy, E [1, 2]. Unfortunately there is a dearth of methods of determination of the order of kinetics in the literature. In a recent work, it has been shown by Singh et al [3] that a rough estimation of E is possible from symmetry factor in conformity with the prescriptions of Chen [4] and Chen and Kirsh [5]. But the accuracy of this method is limited by the non-uniqueness of symmetry factor. Recently, based on the peak shape method of Singh et al [6],

Singh et al [7] has suggested a method for the determination of the order of kinetics by taking into account the non-uniqueness of E for a particular order of kinetics. This method of Singh et al [7] has solved a longstanding problem of determination of the order of kinetics. We hereafter denote the peak shape methods of Singh et al [6,7] as modified peak shape (MPS) method which enables simultaneous determination of activation energy and the order of kinetics. Apart from modified peak shape method, another such method which enables simultaneous determination of activation energy and the order of kinetics is the Kirsh method suggested by Kirsh [8] that uses the area of TL peaks and analysed in details by Karmakar et al [9].

The simplest empirical analytical model of TL is the three-parameter model [1,2], commonly known as GOK model in which the parameters are activation energy (E), the order of kinetics (b) and the frequency factor (s) as mentioned earlier. But starting from a simple band picture of solid,



containing a single kind of electron trap and single kind of hole trap and utilizing the well-known process of thermal de trapping, it is not possible to derive the fundamental TL equation[1,2]. In some classic cases[10-14], anomalous results have been obtained by using the GOK model. These cases indicate the necessity to go beyond the GOK model. The main problem of this model is the non-inclusion of the effects of thermally disconnected deep traps (TDDT), the necessity of the inclusion of the effects of which has been pointed out Fain et al[15]. It is well-known [1, 2, 5] that the effects of TDDT's can be incorporated in the analysis of TL process by using a set of coupled differential equations. In this type of formulation, a number of models namely (i) One trap one recombination centre (OTOR)[16] model (ii) Interactive multitraps system (IMTS)[17,18] etc. have been developed to study TL. In IMTS model, at the time of heating, TDDT's capture free carriers.

In the present work, we critically analyse the applicability of the modified peak shape method[6,7] and area method suggested by Kirsh[8] by applying them to numerically computed TL peaks different models of increasing complexities namely GOK, OTOR and IMTS models of Thermoluminescence. To check validity of MPS and Kirsh methods for the determination of the activation energy and the order of kinetics, we have also analysed the experimental TL glow curves of β -irradiated quartz [19].

2. Methodology

Singh *et al* [6] have suggested a method of the determination of activation energy by using the expression of the type

$$E = [(C_0 + C_1\mu_g + C_2\mu_g^2)kT_m^2] / \omega + (D_0 + D_1\mu_g + D_2\mu_g^2)kT_m \quad (1)$$

The coefficients C_i, D_i ($i = 0,1,2$) are regression constants; k is the Boltzman constant and $\omega = T_2 - T_1$, the full width of TL peak. The coefficients C_i, D_i ($i = 0,1,2$) are found to depend on $u_m = E/kT$. In a subsequent paper, Singh et al[7] have extended the method[6] for the determination of the order of kinetics. So both activation energy and the order of kinetics can be determined by using MPS method due Singh et al[6,7].

In the area method[8] suggested by Kirsh, simultaneous determination of both the activation energy and the order of kinetics is done by using the

area of the glow peak. The basic equation of the method is

$$\frac{\Delta \ln(I)}{\Delta \ln(n/n_0)} = b - \frac{E}{k} \left[\frac{\Delta \ln(1/T)}{\Delta \ln(n/n_0)} \right] \quad (2)$$

Here Δ represents the difference between any two points of the glow curve. n_0 and n are initial number of trapped carriers and number of trapped carriers at any instant t . T is the temperature at time t . I is the TL intensity corresponding to temperature T . From the above equation it is evident that b is the intercept of the linear plot of $\Delta \ln(I) / \Delta \ln(n/n_0)$ against

$\Delta(1/T) / \Delta \ln(n/n_0)$ and E can be determined from its slope. This method is called area method because n/n_0 is related to the area of TL peak.

In GOK model for a linear heating scheme, the TL intensity (I) can be expressed as[4]

$$I = (n/n_0)^b s n_0 \exp(-E/kT) \quad (3)$$

The linear heating scheme considered is represented by the equation

$$T = T_0 + \beta t \quad (4)$$

where T_0 is the initial temperature at $t = 0$, T is the temperature at any time t and β is the constant heating rate.

Going beyond the GOK model, the basic set of coupled differential equations[1,2,5] of TL process for linear heating scheme is given by [1,16]

$$\beta \frac{dn}{dT} = -sn \exp\left(-\frac{E}{kT}\right) + A_n n_c (N - n) \quad (5)$$

$$\beta \frac{dn_c}{dT} = sn \exp\left(-\frac{E}{kT}\right) - A_n n_c (N - n) - n_c n_h A_h$$

6)

$$\beta \frac{dm}{dT} = A_m n_c (M - m) \quad (7)$$

$$I = -\beta \frac{dn_c}{dT} \quad (8)$$

where n_c and n are the instantaneous concentration of free electrons in the conduction band and trapped electrons in electron traps respectively; Furthermore N is the concentration of traps and n_h



is the hole concentration in recombination centers (hole traps). A_n and A_h respectively are proportional to the cross sections of free electron retrapping and of free electron radiative recombination process. A_m is proportional to the cross-section of the electron capture by the TDDT's., M is the concentration of TDDT's and m is the concentration of electrons in TDDT's. The charge neutrality condition is given by $n_h = n + m + n_c$ (9)

In OTOR model , the presence of TDDT's are totally neglected i.e., $m=0$ and the equations (9) , (5) and (6) can be expressed as

$$n_h = n + n_c \quad (10)$$

$$\beta \frac{dn}{dT} = -sn \exp\left(-\frac{E}{kT}\right) + A_n n_c (N - n)$$

$$\beta \frac{dn_c}{dT} = sn \exp\left(-\frac{E}{kT}\right) - A_n n_c (N - n) - n_c (n + n_c) A_h \quad (12)$$

In IMTS model, the corresponding set of coupled differential equations are[18]

$$\beta \frac{dn}{dT} = -ns \exp(-E/kT) + n_c (N - n) A_n \quad (13)$$

$$\beta \frac{dn_c}{dT} = ns \exp(-E/kT) - n_c (N - n) A_n - n_c (M - m) A_m - n_c (m + n + n_c) A_h \quad (14)$$

$$\beta \frac{dm}{dt} = n_c (M - m) A_m \quad (15)$$

$$I = -\beta \frac{dn_h}{dT} = n_c (m + n + n_c) A_h$$

(16)

In the present paper, we have computed synthetic TL curves in GOK, OTOR and IMTS models and

checked the suitability of MPS and Kirsh methods for these curves. Then the experimental TL glow curves of β -irradiated quartz[19] are considered and MPS and Kirsh methods are applied to them to obtain kinetic parameters.

3. Results and Discussion:

We consider the application of both MPS and Kirsh methods to some numerically computed GOK TL peaks of different orders of kinetics for two input values of frequency factor S (10^8 sec^{-1} and 10^{12} sec^{-1}). The corresponding input value of activation energy E_{in} is 1 eV. The values of the activation energy and the order of kinetics as calculated by using by modified peak shape and Kirsh method are denoted by E_{MPS} , b_{MPS} , E_K and b_K . From Table 1., it is found that for all cases considered, the values of E_{MPS} , b_{MPS} , E_K and b_K are in close agreement with the corresponding input values of E_{in} , b_{in} of E and b respectively.

Table 1. Values of activation energy and the order of kinetics as calculated by modified peak shape Method and Kirsh method for numerically generated



TL peaks based n GOK model corresponding to linear heating rate of 1 Ksec⁻¹. $E_{in} = 1eV$

s_{in} (sec ⁻¹)	b_{in}	$T_m(K)$	E_{MPS} (eV)	b_{MPS}	E_K (eV)	b_K
10 ⁸	0.7	537.1	0.999	0.701	0.99	0.699
	1.0	536.5	0.996	0.997	0.99	0.999
	1.5	535.6	0.998	1.497	0.99	1.498
	2.0	534.7	0.995	1.998	0.99	1.997
	2.5	533.9	0.998	2.498	0.99	2.495
10 ¹²	0.7	384.8	0.999	0.695	0.99	0.703
	1.0	384.6	0.997	1.001	0.99	0.998
	1.5	382.2	0.995	1.498	0.99	1.502
	2.0	383.8	0.997	2.001	0.99	1.986
	2.5	383.5	0.998	2.504	0.99	2.495

Next we have computed TL peaks by solving the set of coupled differential equations corresponding to OTOR and IMTS models. The set of coupled differential equations have been solved by fourth order Runge-Kutta method as modified by Gill [20]. The convergence is very slow and depends critically on step size [21]. In the present case, the values of step size range between 0.005 K and 0.001 K. As a check of our computer code, we have reproduced the results of Singh [21], Kelly et al [22] and Sakurai and Gartia[23]. For numerical computation of TL curves by using set of coupled differential equations, the initial values of n and m denoted respectively by n_0 and m_0 have been computed under the condition of filling of traps according to a saturating exponential function with filling rate constant proportional to A_n and A_h . The results are presented in Table 2. For all computer generated TL peaks we have taken $E = 1 eV$, $S = 10^{12} sec^{-1}$, $N = 10^{12} cm^{-3}$ and $\beta = 1 Ksec^{-1}$. It is evident that for IMTS model the calculated values of activation energy E_{MPS} by using MPS method are in good agreement with the input values of E used in numerical computation. The same is true for OTOR model. In Table 2, the values of activation. energy E_K as calculated by using the area method of

Kirsh is also depicted. Both E_{MPS} and E_K are accurate within a few percent and are in good agreement among themselves.

Unlike GOK model, the order of kinetics does not occur explicitly in different models considered in the present work. However, kinetics order may still be considered as some sort of gross parameter arising as a result of interplay between the contribution of microscopic and macroscopic factors. In Table 2, we have also presented the values the order of kinetics b_{MPS} and b_K as calculated by modified peak shape method [7] and area method [8]. The mutual agreement between the values of b_{MPS} and b_K shows the reliability of both the methods in connection with the determination of the order of kinetics. From Table 2, we observe the strong variation of the order of kinetics with dose. In fact, the kinetic order determined by the values of b and might be altered by the approximate variation of dose, a point mentioned by Singh et al [7]. Experimentally this variation has been observed independently by Pokormy and Ibarra [24] and Gartia et al [25]. These variations in fact represents the shift of the order of kinetics with dose, because peak temperature depends on the order of kinetics for a particular value activation energy.

Table 2. Activation energies and the order of kinetics of some numerically computed peaks of TL by using modified peak shape and Kirsh method



MODEL	n_0 cm ⁻³	m_0 cm ⁻³	A_t cm ³ s ⁻¹	A_m cm ² s ⁻¹	A_h cm ² s ⁻¹	E_K eV	b_K	E_{MPS} eV	b_{MPS}
OTOR	10 ¹²	0	10 ⁻¹⁰	N.A.	10 ⁻⁷	0.9902	0.9915	0.989	0.9942
OTOR	10 ¹²	0	10 ⁻¹⁰	N.A.	10 ⁻⁷	1.005	1.2542	1.007	1.2648
OTOR	3 × 10 ⁹	0	10 ⁻¹⁰	N.A.	10 ⁻⁷	1.0031	2.1007	1.002	2.1012
OTOR	2 × 10 ⁹	0	10 ⁻¹⁰	N.A.	10 ⁻⁷	1.0059	1.5614	1.006	1.5532
OTOR	10 ⁸	0	10 ⁻¹⁰	N.A.	10 ⁻⁷	1.002	1.875	1.003	1.876
OTOR	10 ¹²	0	10 ⁻⁷	N.A.	10 ⁻⁷	1.0102	1.5872	1.010	1.6321
OTOR	10 ¹²	0	10 ⁻⁷	N.A.	5 × 10 ⁻⁸	1.0006	2.095	1.007	2.094
IMTS	10 ¹¹	10 ¹²	10 ⁻⁹	10 ⁻⁹	10 ⁻⁹	1.0032	1.005	1.004	1.004
IMTS	10 ¹¹	10 ⁹	10 ⁻⁹	10 ⁻⁹	10 ⁻⁹	0.951	1.745	0.952	1.741
IMTS	3.94 × 10 ¹¹	9.93 × 10 ¹¹	10 ⁻⁹	10 ⁻⁸	10 ⁻⁹	1.0148	1.0557	1.014	1.0559
IMTS	5 × 10 ¹¹	6.7 × 10 ¹¹	10 ⁻⁹	10 ⁻¹⁰	10 ⁻⁹	1.0163	1.7741	1.015	1.2899
IMTS	10 ¹⁰	10 ⁹	10 ⁻⁸	10 ⁻⁹	10 ⁻⁸	1.0852	0.8347	1.017	1.0101
IMTS	10 ¹²	9.93 × 10 ¹¹	10 ⁻⁹	10 ⁻¹⁰	10 ⁻¹¹	0.985	0.882	0.988	0.887
IMTS	10 ¹²	6.32 × 10 ¹¹	10 ⁻⁹	10 ⁻¹⁰	10 ⁻¹¹	0.985	0.838	0.983	0.834

. N. A. means not applicable

(b_{cf}) for different peaks[19].

Finally, we consider experimental TL glow curves of β -irradiated quartz[19]. The TL glow curve of Quartz (irradiated at room temperature with irradiation dose of 8.33Gy) are recorded with a heating rate of 5 Ksec⁻¹. Using computerized glow curve deconvolution technique (CGCD), based on Chen's general order kinetic formalism, (Chen and Kirsh, 1981), eleven peaks were obtained. As both the modified peak shape method and Kirsh method are applicable to a single peak, we have adapted the technique of El-Hafez *et al.*[26] in this multipeak system. To analyse the glow curves of β -irradiated quartz, a successful fit of previous peak is followed by subtraction from entire glow curve. Table 3. shows the curve fitted value (E_{cf}) of activation energies together with those of the order of kinetics

Table 3 also depicts the values of activation energies and the order of kinetics of some experimental TL peaks of β -irradiated quartz as calculated by the modified peak shape method[6,7] together. The corresponding agreement among themselves point at the suitability of the modified peak shape method and the Kirsh method for the experimental TL peaks of β -irradiated quartz.



Peak No.	$T_m (K)$	$E_{cf} (eV)$	b_{cf}	$E_{MPS} (eV)$	b_{MPS}	$E_K (eV)$	b_K
1	413	0.96	1.05	0.94	1.04	0.95	1.03
2	434	1.01	1.15	1.02	1.16	0.99	1.15
3	476	1.10	1.10	1.10	1.11	1.09	1.12
4	503	1.18	1.95	1.15	1.96	1.17	1.94
5	535	1.25	1.05	1.26	1.06	1.27	1.04
6	566.5	1.32	1.32	1.30	1.34	1.30	1.33
7	604.5	1.43	1.70	1.41	1.71	1.45	1.72
8	646	1.52	1.70	1.52	1.72	1.51	1.73
9	699	1.65	1.70	1.66	1.69	1.67	1.68
10	770	1.82	1.8	1.81	1.78	1.79	1.83
11	822	1.94	1.8	1.95	1.81	1.81	1.82

Table 3. Determination of activation energies and the order of kinetics of some experimental TL peaks of β -irradiated quartz

4. Conclusion:

We have studied the suitability of modified peak shape method [6,7] and area method of Kirsh[8] in light of different models of TL namely, GOK,OTOR and IMTS. The values of activation energy and the order of kinetics as calculated by the two methods under consideration to the numerically computed TL curves according to the models mentioned above are in fair agreement with the input values. Finally, the activation energies and the order of kinetics of experimental TL peaks of β irradiated quartz [19] agree closely with those calculated by modified peak shape method and Kirsh method. Keeping in mind the experimental errors involved in the determination of the order of kinetics and activation energies, we can conclude that these two methods can be used irrespective of the models of TL for the determination of activation energies and the order of kinetics.

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