Evaluation of kinetic parameters from thermoluminescence glow curves

Mahua Karmakar[1]*, Bikash Kumar Sarkar[2], Supriya Barman[3], P S Mazumdar[1],
S Dorendrajit Singh[4], W Sambhunath Singh[5] and Manabesh Bhattacharya[6]

[1]Department of Physics, A P C College, New Barrackpore, Kolkata 700 131, West Bengal, India
[2]Department of Physics, M D Mahavidyapith, Birati, Kolkata-700 051, West Bengal, India
[3] Bhangar Balika Vidyalaya, Bhangar, 24 Parganas (South), West Bengal, India
[4]Department of Physics, Manipur University, Canchipur, Imphal 795 003, Manipur, India
[5] Department of Physics, Manipur College, Singjamei Imphal-795 008, Manipur, India
[6] Department of Physics, K N College, Berhampur 742 101, West Bengal, India

E mail   mahua_apc@yahoo com

Abstract   In the present paper two methods of determination of trapping parameters from thermoluminescence glow curves are considered One is due to Kirsh and the other is suggested by Vejnovic et al By taking into account both the computer generated and the experimental TL peaks, it is established that the Kirsh method is superior to that of Vejnovic et al The possible application of Kirsh method to the case of temperature dependent frequency factor is also studied

Keywords : Thermoluminescence, trapping parameters, temperature dependent frequency factor

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1. Introduction

Thermoluminescence (TL) is often used for studies of trapping levels is solids, in particular for the evaluation of trap depth or the activation energy [1]. The study remains active because of its applications in the field of dosimetry and dating [1,2]. A number of methods [1] are currently been applied for the evaluation of the trapping parameters from a TL glow peak *i.e.* activation energy (E), order of kinetics (b) and frequency factor (s). Vejnovic *et al* [3] proposed a method of determination of TL trapping parameters. In the present paper

Corresponding Author

the method of Vejnovic *et al* is denoted by the acronym VPRD VPRD method makes use of a single expression for activation energy The main difficulty of using such expression is requirement of prior knowledge of order of kinetics It seems that Vejnovic *et al* is not aware of this fact pointed out by Gartia *et al* [4] Moreover they have not taken note of the existence of a number of expressions of activation energy [5,6]

Kirsh [7] suggested a method of evaluation of TL trapping parameters The method is simple and straight forward in the sense that unlike other conventional methods of determination of trapping parameters such as peak shape, initial rise and various heating rates [8], it permits simultaneous evaluation of order of kinetics b and activation energy E In the present paper a critical comparison of VPRD method and Kirsh method has been done Finally an attempt has been made to adjudge the validity of Kirsh method for the case of temperature dependent frequency factor [1,8]

2. Theory

The expression for TL intensity I can be expressed as [7]

$$1 = -\frac{dn}{dt} \tag{1}$$

with
$$\frac{dn}{dt} = \left(\frac{n}{n_0}\right)^b sn_0 \exp\left(\frac{-E}{kT}\right) \tag{2}$$

where T is the temperature at time t, n and n_0 are respectively, the number of trapped carriers at time t and initial number of trapped carriers, k is Boltzmann constant, b is the order of kinetics For a linear heating profile given by the eq [8]

$$T = T_0 + \beta t \tag{3}$$

where β is the linear heating rate and T_0 is the initial temperature Equation (2) can be recast as [4]

$$\frac{I}{I_m} = \exp\left[(u_m - u) + F(u, u_m)\right] \qquad (b = 1) \tag{4}$$

and

$$\frac{I}{I_m} = \exp(u_m - u)\left[1 - \frac{b-1}{b}F(u, u_m)\right]^{-\frac{b}{b-1}} \qquad (b \neq 1) \tag{5}$$

I_m is intensity corresponding to the peak temperature T_m

$$F(u, u_m) = u_m^2 \exp(u_m)\left[\frac{E_2(u_m)}{u_m} - \frac{E_2(u)}{u}\right] \tag{6}$$

With $u = E/kT$ and $u_m = E/kT_m$

$E_2(u)$ is the second exponential integral [9]

Following (2) one can write [7]

$$\frac{n}{n_0} = \frac{A(T)}{\beta} \tag{7}$$

$A(T)$ is the area of the peak from temperature T upto its end point temperature T_e and is given by

$$A(T) = \int_T^{\infty} I(T') \, dT' \tag{8}$$

From eqs (2) and (3) for any two points of the TL curve [7]

$$\frac{\Delta \ln(I)}{\Delta \ln(n/n_0)} = b - \frac{E}{k} \frac{\Delta \ln(I/T)}{\Delta \ln(n/n_0)} \tag{9}$$

where Δ represents the difference between any two points of the TL curve n/n_0 is calculated from eq (7) From eq (9) it follows that a plot of $\Delta\ln(I)/\Delta\ln(n/n_0)$ against $\Delta\ln(1\,T)/\Delta\ln(n/n_0)$ will give a straight line of slope $-(E/k)$ and intercept b Thus Kirsh method allows simultaneous evaluation of b and E Knowing b and E the frequency factor s can be obtained from the equation [8]

$$s = \beta \left| \frac{bkT_m^2}{E} \exp\left(\frac{E}{kT_m}\right) - (b-1) \int_{T_0}^{T_m} \exp\left(\frac{-E}{kT}\right) dT \right|^{-1}$$

Now according to VPRD method expressions for trapping parameters are given by [3]

$$E = \frac{bkT_m^2}{\prime_{eff}} \tag{10}$$

and

$$b = \frac{-A_1 + \sqrt{A_1^2 - 4A_0 A_2}}{2A_0} \tag{11}$$

with

$$A_0 = -\ln\left[\frac{\prime_{eff}}{W_{eff}}\right] - 0\,2 \tag{12}$$

$$A_1 = -0\,592\,\ln\left[\frac{\delta_{eff}}{w_{eff}}\right] - 1378 + \frac{152\delta_{eff}}{T_m} \tag{13}$$

and $\qquad A_2 = 0\,9\,\dfrac{\delta_{eff}}{T_m}$ $\hspace{5cm}$ (14)

where δ_{eff} and w_{eff} are respectively, the areas of the falling side and the whole peak s has been found out by using the approximate equation

$$s = \frac{\beta E}{kT_m^2}\exp\left(\frac{E}{kT_m}\right)\left[1 + (b-1)\frac{2kT_m}{E}\right]^{-1} \tag{15}$$

Normally in the analysis of the TL curves, the frequency factor is assumed to be temperature independent But this assumption needs modification in view of temperature dependence of capture cross-sections [1,7,8,10,11] As a results s varies as $T^a(-2 < a \le 2)$ i e we can write $s(T) = s_0\,T^a$ where s_0 is a constant For the case of temperature dependent frequency factor the analogues of equations (4)–(6) are given by [12]

$$\frac{I}{I_m} = \left(\frac{u_m}{u}\right)^a \exp\left[(u_m - u) + F(u, u_m)\right] \qquad (b = 1) \tag{16}$$

$$\frac{I}{I_m} = \left(\frac{u_m}{u}\right)\exp(u_m - u)\left[1 - \frac{b-1}{b}F(u, u_m)\right]^{-\frac{b}{b-1}} \quad (b \ne 1) \tag{17}$$

With $\quad F(u, u_m) = \left(u_m^2 + au_m\right)u_m^a\,\exp(u_m)\left[\dfrac{E_{a+2}(u_m)}{u_m^{a+1}} - \dfrac{E_{a+2}(u)}{u^{a+1}}\right]$

Where $E_n(u)$ is the n-th order exponential integral [9]

3. Results and discussion

It is clear from eq (7) that in order to find n/n_0 one has to compute the area of the peak which requires the computation of the integral $\int_T^{T_e} I(T')\,dT'$ (T_e being the end point temperature) Now considering the case of non first order kinetics ($b \ne 1$) [eqs (5) and (6)] the area of the portions of the peak from temperature T to the end point temperature T_e is given by

$$A(T) = \int_{T}^{T_e} \exp(u_m - u') \left[1 - \frac{b-1}{b} F(u', u_m) \right]^{-\frac{b}{b-1}} dT' \qquad (19)$$

T_e is obtained by solving the equation $I(T_e) = 0$ $(T_e > T_m)$ numerically by using Newton, McAuley method [13] Changing the independent variable from T to u $(= E/kT)$ eq (19) can be expressed as

$$A(u) = \frac{E}{k} \int_{u}^{u_m} \exp(u_m - u') \left[1 - \frac{b-1}{b} F(u', u_m) \right]^{-\frac{b}{b-1}} u'^{-2} du' \qquad (20)$$

Integral occurring in eq (20) has been evaluated by using Gauss Legendre quadrature method [14] with range (u, u_e) being split into a number of subranges The integral over each subranges has been carried out by using 16-point Gauss Legendre quadrature The second exponential integral has been evaluated [15] by using its continued fraction representation [16] For the first order kinetics similar numerical technique has been followed

As a check of our computer code we have reproduced the values of δ_{eff} and w_{eff} of numerically computed TL peaks reported by Vejnovic et al [3] The order of kinetics (b) and activation energy (E) have been found out by using the technique of standard least square regression [17]

In Table 1 we present the trapping parameters of a number of computer generated TL peaks considered by Vejnovic et al [3] E_{in}, E_k and E_v denote respectively the input

Table 1. Trapping parameters of some numerically computed TL peaks corresponding to the linear heating rate (β = 0 5K/sec)

E_{in}(eV)	b_{in}	S_{in} (sec^{-1})	E_k (eV)	b_k	s_k(sec^{-1})	E_v (eV)	b_v	s_v (sec^{-1})
1 5	2 5	10^{13}	1 608	2 524	1 166×10^{13}	1 599	2 493	9 86×10^{12}
1 6	1 9	10^{13}	1 601	1 908	1 017×10^{13}	1 600	1 896	9 90×10^{12}
0 4	1 5	10^{13}	0 399	1 501	9 380×10^{12}	0 400	1 498	9 93×10^{12}
1 6	1 5	10^{9}	1 601	1 510	1 022×10^{9}	1 600	1 498	9 95×10^{8}
0 4	1 5	10^{9}	0 400	1 513	1 032×10^{9}	0 400	1 498	9 95×10^{8}
0 1	1 5	10^{9}	0 100	1 511	1 017×10^{9}	0 100	1 498	9 95×10^{8}
0 1	0 7	10^{8}	0 090	0 691	8 904×10^{7}	0 100	0 700	1 00×10^{8}
1 6	0 7	10^{5}	1 586	0 686	8 524×10^{4}	1 600	0 700	1 00×10^{5}
0 4	1 9	10^{5}	0 396	1 893	8 679×10^{4}	0 400	1 894	9 95×10^{4}
0 1	1 9	10^{5}	0 099	1 885	8 259×10^{4}	0 100	1 894	9 95×10^{4}
0 1	2 5	10^{5}	0 098	2 450	7 269×10	0 100	2 485	9 91×10^{4}

values of activation energy, activation energy as calculated by Kirsh method and activation energy as calculated by VPRD method b_{in}, b_k and b_v, s_{in}, s_k and s_v are the corresponding values of order of kinetics and frequency factor respectively A close inspection of Table 1 reveals that in most of the cases the values of the trapping parameters as calculated by the Kirsh method are more closer to the input values than those of VPRD method

Encouraged by our findings in the case of numerically computed peaks we consider well analyzed experimental first order 165 5°C TL peak (β = 25°C/min) [5] of Ca doped KCl, X-irradiated at room temperature followed by thermal cleaning upto 150°C and 320°C second order TL peak of bluish green microline (β = 40°C/min) [18] In Table 2 we depict the results of application of Kirsh method and VPRD method to the aforesaid experimental TL peaks E_{cf}, b_{cf} and S_{cf} are the values of trapping parameter obtained by using the rigorous method of curve fitting It is evident from Table 2 that also in the case of experimental TL peaks the values of the trapping parameters as calculated by using Kirsh method show a better overall agreement with the curve fitted values than those by using VPRD method

Table 2. Trapping parameters of some experimental TL peaks

E_{cf}(eV)	b_{cf}	S_{cf} (sec^{-1})	E_k (eV)	b_k	s_k(sec^{-1})	E_v (eV)	b_v	s_v (sec^{-1})
1 36	1 0	1 46×10^{14}	1 36	1 00	1 53×10^{14}	1 36	1 00	1 46×10^{14}
1 42	2 0	3 44×10^{10}	1 43	2 01	3 84×10^{10}	1 42	2 00	3 41×10^{10}

Finally we apply Kirsh method to some computer generated TL peaks with the temperature dependent frequency factor as reported by Flemming [19] A perusal of Table 3 shows that in this case the error in the determination of the activation energy is of the order of 10% as in the case of other methods of analysis such as peak shape, various heating rates and initial rise [8] We get good agreement in the values of b This is because of the fact that the symmetry factor μ_g of a TL peak with temperature dependent frequency factor is not much sensitive to value of temperature exponent a [12, 19] According to Chen and Kirsh [8] the activation energy obtained in the case of temperature dependent frequency factor should be corrected by subtracting akT_m from its calculated value In

Table 3. Trapping parameters of some numerically computed TL peaks ith temperature dependent frequency factor All peaks correspond to a linear heating rate of 0 42 K/s

a	T_m(K)	E_{in}(eV)	b_{in}	$(s_0 T^a{}_m)_{in}$ (sec^{-1})	E_k (eV)	b_k	$(s_0 T_m{}^a)_k$ (sec^{-1})	E_{ck} (eV)
2	595	1 303	2 0	1 27×10^{10}	1 395	1 981	1 27×10^{10}	1 292
2	595	1 497	2 0	1 27×10^{10}	1 404	2 011	1 27×10^{10}	1 507
2	580	0 409	1 0	158 63	0 489	0 963	151 82	0 389
2	580	0 591	1 0	158 63	0 510	1 037	158 97	0 610

table 3 we also present the corrected value of E_k given by $E_{ck} = E_k - akT_m$ as obtained by following the prescription of Chen and Kirsh They are in good agreement with input value of E

4. Conclusion

In the present paper a comparative study of Kirsh method [7] and VPRD method [3] for the determination of TL trapping parameters have been made by considering both computer generated and experimental TL peaks In general, the prediction of Kirsh method is found to be better than those of VPRD method As mentioned by Vejnovic *et al* [3] themselves VPRD method does not give good results for $b = 0\ 7$ but Kirsh method gives good results even for $b = 0\ 7$ This is because of the fact that Kirsh method has a sound mathematical basis resulting directly from basic TL equations whereas the development of VPRD method requires some approximation Moreover as we have already noted that unlike other conventional method of determination of trapping parameters such as initial rise, various heating rates and peak shape Kirsh method admits of simultaneous evaluation of activation energy (E) and order of kinetics (b) It is gratifying to note that Kirsh method can also be applied to the case of temperature dependent frequency factor

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