

Determination of activation energy and order of kinetics of thermoluminescence peaks recorded with hyperbolic heating profile

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Abstract: A set of expressions are presented for the evaluation of activation energy of thermoluminescence (TL) peaks recorded with hyperbolic heating profile. In this method, along with the conventional half intensity points, the peak widths at signal levels equal to 0.8 and 0.95 of the peak height are chosen to reduce the effects of satellite peaks. A method of estimation of the order of kinetics of a TL peak by using its symmetry factor is also proposed. The present method has been applied to computer generated TL peaks and encouraging results have been obtained.

Keywords: Thermoluminescence, Hyperbolic heating scheme, Activation energy, Order of kinetics

1. Introduction:

Thermally Stimulated Luminescence (TSL) popularly known as thermoluminescence (TL) is the emission of light on heating a previously irradiated semiconducting or insulating solid. Usually a suitable ionizing radiation such as X-rays, γ - rays or β - rays is used for irradiating the solid. TL has been applied to the fields of Dosimetry, Dating, and trapping level studies of TL emitting solids [1, 2]. Usually TL is analyzed by using three parameters kinetic order model (KOM) [1, 2]. The trapping parameters are order of kinetics (b) activation energy (E) and frequency factor (s). Peak shape method [1-4] is one of the simplest methods of the determination of activation energy of TL peaks.

Usually TL is recorded under linear heating scheme (LHS) [1, 2]; but there are a number of works [5-10] on TL corresponding to hyperbolic heating scheme. Christodoulides [9] has done an exhaustive work on peak shape method in TL corresponding to hyperbolic heating scheme (HHS). But his work has to be refabricated in a more usable form, so that it can be used by TL workers. For example in his work, he has used the fractional intensity point $x = 0.25$ ($x = \frac{I}{I_m}$, I is the intensity at any temperature T and I_m is the peak intensity); but we know this fractional intensity point lies in the lower half of the peak and hence can be seriously affected by neighbouring

satellite peaks. As a result it might not be possible to accurately determine the rising and falling side temperatures corresponding to $x = 0.25$. So the calculated activation energy will be in error. In the present work, we have chosen the fractional intensity points $x = 0.50, 0.80, 0.95$. In the usual peak shape method half intensity points ($x = 0.50$) are considered. In the present work apart from the half intensity points we also consider fractional intensity points $x = 0.80$ and 0.95 because these points lie in the upper half of the peak where the effect of satellite peaks will be less. We have also suggested a relation between the symmetry factor $\mu_g(x)$ corresponding to the fractional intensity x and order of kinetics (b). As a result knowing $\mu_g(x)$, b can be estimated. We also suggest a set of expressions for the determination of activation energy. We have tested the suitability of these expressions by applying them to computer generated TL peaks.

2. Methodology:

Following Christodoulides [9, 10] one can write

$$I(T) = -\frac{dn}{dt} = s \frac{n^b}{N^{b-1}} \exp\left(-\frac{E}{kT}\right) \quad (1)$$

$I(T)$ is the TL intensity at the temperature T , n is the concentration of trapped electrons at time t , N is total concentration of traps, k is the Boltzmann Constant, E is the activation energy, b is the order of kinetics and

s is the frequency factor. The HHS can be represented as

$$\frac{1}{T} = \frac{1}{T_0} - \beta' t \quad (2)$$

where T_0 is the temperature at time $t = 0$ (initial temperature),

T is the temperature at time t , β' is a constant.

The heating rate in HHS at temperature T is given by

$$\frac{dT}{dt} = \beta' T^2 \quad (3)$$

So heating rate in HHS is not constant but is proportional to T^2 ; because of this HHS is also called quadratic heating scheme [1, 2].

From equations (1) and (3) we get first order kinetics ($b = 1$)

$$I = sn_0 \exp\left(-\frac{E}{kT}\right) \exp\left(-\frac{s}{\beta'} J(T_0, T)\right) \quad (4)$$

$J(T_0, T)$ is the temperature integral denoted by

$$\int_{T_0}^T \frac{\exp\left(-\frac{E}{kT'}\right)}{T'^2} dT' \quad (5)$$

For non first order kinetics ($b \neq 1$) using equations (1) and (3) we get for a saturated ($n_0 = N$) TL peak,

$$I(T) = sn_0 \exp\left(-\frac{E}{kT}\right) [1 + (b - 1) \frac{s}{\beta'} J(T_0, T)]^{-\frac{b}{b-1}} \quad (6)$$

Equation (6) is not valid $b = 1$ but using the well known limit [12]

$$\lim_{x \rightarrow 0} (1 + x)^{\frac{1}{x}} = e \quad (7)$$

it can be shown that as $b \rightarrow 1$ equation (6) reduces to equation (4).

Using (4) and (6) one can evaluate $\frac{dI}{dT}$. If T_m is the peak temperature

$$\left(\frac{dI}{dT}\right) = 0, \text{ for } T = T_m \quad (8)$$

The peak temperature T_m both for first order $b = 1$ and non first order kinetics $b \neq 1$

$$\frac{\beta' E}{k} = s \exp\left(-\frac{E}{kT_m}\right) \quad (9)$$

From equation (9) it is evident that the maximum condition for HHS is independent for the order of kinetics b . For LHS the maximum condition depends on b but the dependence is weak. The maximum condition for LHS for non first order kinetics can be expressed as [3]

$$\frac{\beta' E}{kT_m^2} = s \exp\left(-\frac{E}{kT_m}\right) \left[1 + (b - 1) \frac{2kT_m}{E} \right] \quad (10)$$

For actual TL peaks, the quantity $u_m = \frac{E}{kT_m}$ varies from 10 to 100 so that the contribution of second

term within the braces in equation (10) is usually small compared to 1. As a result, equation (10) is almost independent of the order of kinetics b .

The temperature integral can be evaluated as $J(T_0, T)$ [11]

$$J(T_0, T) = \frac{k}{E} [\exp\left(\frac{-E}{kT}\right) - \exp\left(\frac{-E}{kT_0}\right)] \quad (11)$$

Now eliminating $\frac{s}{\beta'}$ between equations (4) and (9) and using equation (11) one gets the following expression for fractional intensity x for first order kinetics ($b = 1$)

$$x = \frac{I}{I_m} = \exp[u_m - u + F(u, u_m)] \quad (12)$$

Similarly eliminating $\frac{s}{\beta'}$ between equations (6) and (9) and using equation (11) one gets the following expression for fractional intensity x for non first order kinetics ($b \neq 1$)

$$x = \frac{I}{I_m} = \exp(u_m - u) [1 - \frac{b-1}{b} F(u, u_m)]^{-\frac{b}{b-1}} \quad (13)$$

with

$$u = \frac{E}{kT} \quad \text{and} \quad u_m = \frac{E}{kT_m} \quad (14)$$

and

$$F(u, u_m) = 1 - \exp(u_m - u) \quad (15)$$

Using equations (11) and (12) one can evaluate temperatures T_{x1} and T_{x2} corresponding to fractional intensity x in the rising and falling sides of the TL peak for arbitrary order of kinetics b . i.e.

$$T = T_{x1} \text{ for } T_{x1} < T_m \left(\frac{I}{I_m} = x\right)$$

$$T = T_{x2} \text{ for } T_{x2} > T_m \left(\frac{I}{I_m} = x\right)$$

We also define

$$u_{x1} = \frac{E}{kT_{x1}} \text{ and } u_{x2} = \frac{E}{kT_{x2}} \quad (16)$$

By using the standard technique of nonlinear regression [13] it is possible to write

$$u_{x1} - u_m = A_{\tau x}^{(0)} + A_{\tau x}^{(1)} b + A_{\tau x}^{(1)} b^2 \quad (17)$$

$$u_m - u_{x2} = A_{\delta x}^{(0)} + A_{\delta x}^{(1)} b + A_{\delta x}^{(1)} b^2 \quad (18)$$

$$u_{x1} - u_{x2} = A_{\omega x}^{(0)} + A_{\omega x}^{(1)} b + A_{\omega x}^{(1)} b^2 \quad (19)$$

It is to be noted that for arbitrary value of x ,

$\tau_x = T_m - T_{x1}$, $\delta_x = T_{x2} - T_m$ and $\omega_x = T_{x2} - T_{x1}$ are respectively rising side half width, falling side half width and full width corresponding to the fractional intensity x . Using equation (16), equations (17-19) can be expressed as

$$E_{\tau x} = \frac{kT_{x1} T_m}{\tau_x} [A_{\tau x}^{(0)} + A_{\tau x}^{(1)} b + A_{\tau x}^{(1)} b^2] \quad (20)$$

$$E_{\delta x} = \frac{kT_{x2} T_m}{\delta_x} [A_{\delta x}^{(0)} + A_{\delta x}^{(1)} b + A_{\delta x}^{(1)} b^2] \quad (21)$$

$$E_{\omega x} = \frac{kT_{x2} T_{x1}}{\omega_x} [A_{\omega x}^{(0)} + A_{\omega x}^{(1)} b + A_{\omega x}^{(1)} b^2] \quad (22)$$

3. Results and Discussions:

For a particular value of $\frac{I}{I_m}$, $u_{x1} = \frac{E}{kT_{x1}}$ and $u_{x2} = \frac{E}{kT_{x2}}$ have been obtained by solving equations (12) and (13) by an iterative method [9] for ($b = 1$) and ($b \neq 1$) respectively. As already mentioned, the coefficients $A_{jx}^{(i)}$ ($i = 0, 1, 2$; $j = \tau_x, \delta_x, \omega_x$) have been obtained by using the numerical technique of nonlinear regression [13]. The co-efficients are tabulated in Table 1 for $x = 0.5, 0.8$ and 0.95 . Using equations (20-22) activation energy E can be calculated.

The symmetry factor $\mu_g(x)$ can be defined as [9]

$$\mu_g(x) = \frac{u_m - u_{x2}}{u_{x1} - u_{x2}} \quad (23)$$

Again using the technique of nonlinear regression for a particular value of x , $\mu_g(x)$ can be expressed as

$$\mu_g(x) = a_{0x} + a_{1x} b + a_{2x} b^2 \quad (24)$$

The co-efficients a_{ix} ($i = 0, 1, 2$; $x = 0.5, 0.8, 0.95$) are tabulated in Table 2. $\mu_g(x)$ can be obtained from the TL curve under consideration. Knowing $\mu_g(x)$ order of kinetics b can be evaluated from equation (24). The calculated value of b is denoted by b_c . Again using the present sets of formulae, we can calculate $E_{\tau x}$, $E_{\delta x}$ and $E_{\omega x}$ for a particular TL peak. For a particular value of x and b we calculate the average of E_{τ} , E_{δ} and E_{ω} and denote it by E_c . For a particular computer generated peak knowing E_c and b_c , s can be determined from equation (9). The value of s so obtained is denoted by s_c . Hence by using the present method, we can determine all the three trapping parameters E , b and s . The result of the application of the present method to a number of computer generated TL peaks are depicted in Table 3. It is evident from Table 3 that the calculated values of trapping parameters namely E_c, b_c and s_c of E , b and s are in good agreement with the corresponding input values namely E_{in}, b_{in} and s_{in} of the computer generated TL peaks. It is to be noted for linear heating scheme, it is not possible to determine b accurately from $\mu_g(x)$. This is because of the fact for a particular value of x , $\mu_g(x)$ depends weakly on the

quantity $u_m = \frac{E}{kT_m}$ apart from its strong dependence on b . This might lead to a large error about 1-20% in the determination of b by using equation of the type (23) for the LHS [14]. But for hyperbolic heating scheme $\mu_g(x)$ depends uniquely on b . As a result order of kinetics b can be accurately determined by using equation (23).

4. Conclusion:

In the present work we suggest a method of calculation of trapping parameters for TL peaks obtained by using hyperbolic heating profile. The method yields satisfactory results for computer generated TL peaks corresponding to HHS.

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Table 1: Co-efficients $A_{jx}^{(i)}$ ($i = 0, 1, 2$; $j = \tau_x, \delta_x, \omega_x$) occurring in equations (20-22)

x	j	$A_{jx}^{(0)}$	$A_{jx}^{(1)}$	$A_{jx}^{(2)}$
0.5	τ	1.0788	0.4329	-0.0453
	δ	0.1559	0.8638	-0.0301
	ω	1.2347	1.2967	-0.0754
0.8	τ	0.4879	0.2964	-0.0295
	δ	0.1907	0.4416	-0.0278
	ω	0.6785	0.7380	-0.0573
0.95	τ	0.1949	0.1601	-0.0150
	δ	0.1265	0.1941	-0.0149
	ω	0.3215	0.3542	-0.0299

Table 2: Co-efficients a_{ix} ($i = 0, 1, 2$); $x = 0.5, 0.8, 0.95$ occurring in equations (24)

x	a_{0x}	a_{1x}	a_{2x}
0.5	0.2716	0.1543	-0.0200
0.8	0.3697	0.0882	-0.0115
0.95	0.4374	0.0424	-0.0056

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Table 3: Trapping parameters of some computer generated TL peaks by using the present method. The input values are $E_{in} = 1\text{eV}$, $s_{in} = 1. e12$ are common to all the peaks.

Fractional Intensity x	b_{in}	E_{τ} (eV)	E_{δ} (eV)	E_{ω} (eV)	E_c (eV)	b_c	s_c (sec ⁻¹)
0.5	1.0	0.997	0.980	0.990	0.989	0.97	1.13e12
	1.5	1.00	1.01	1.01	1.01	1.52	1.12e12
	2.0	1.00	1.00	1.00	1.00	2.0	1.0e12
0.8	1.0	0.995	0.986	0.991	0.991	0.97	1.16e12
	1.5	1.00	1.01	1.00	1.00	1.52	1.16e12
	2.0	1.00	1.00	1.00	1.00	2.00	1.0e12
0.95	1.0	0.993	0.989	0.989	0.990	0.97	1.5e12
	1.5	1.01	1.01	1.01	1.01	1.53	1.3e12
	2.0	1.00	1.00	1.00	1.00	2.01	1.0e12