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Recent developments on the analysis of thermoluminescence

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Abstract : Thermoluminescence (TL) is a relatively simple but potentially powerful technique to determine the trapping levels in insulating and semiconducting solids. Practically, all the works on the analysis of TL are based on the three trapping parameters *viz.* activation energy (E), frequency factor (s) and order of kinetics (b) These are required for the estimation of the lifetime of the electron in the trap which has practical utility in TL dosimetry and TL dating. Unfortunately, the critics of the analysis of the TL by kinetics formalism fail to realise this. The present review deals with the recent developments in the analysis of TL.

Keywords : Thermoluminescence (TL), activation energy, order of kinetics, frequency factor.

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Plan of the Article

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1. General introduction

1.1. Introductory remarks :

Thermally stimulated luminescence (TSL) commonly known as thermoluminescence (TL) is a common and widespread phenomenon occurring in different substances such as amorphous and polycrystalline materials, single crystals of semiconductors and insulators, minerals, ceramics and also in biological materials like fish scales, bones and dental enamel *etc*. In this phenomenon, light is emitted from a sample during heating as a result of the previous absorption of energy from radiation such as X-rays, γ-rays *etc*. The occurrence of TL during a thermal scan of a previously excited material is probably one of the most direct evidence that we have for the existence of electronic trapping levels in these materials. A thermoluminescence spectrum normally consists of a number of overlapped peaks which are rarely isolated.

Research activities in the area of TL over the years, have developed mainly across three different directions. The first approach is concentrated on the determination of the trapping parameters such as activation energy (E), frequency factors (s) and order of kinetics (b) relevent to the experimental TL glow curve [1,2]. There are various techniques to determine these parameters. These will be discussed in subsequent sections. The second approach is related to studies on defect centres [3,4]. This is quite natural in view of the fact that TL is a sensitive technique capable of detecting very small number of defect levels. The third approach makes use of the capability of deep traps in insulating materials to store charge carriers above room temperature for a long time and its retrieval in a thermal scan of TL. This leads to two main applications of TL in the fields of dosimetry and dating [5–9].

The first theory of TL for first order kinetics was proposed by Randall and Wilkins [10] followed by that of Garlick and Gibson [11] for second order kinetics. Later developments in this area till mid-eighties, have been covered by a number of excellent review articles [12–15] and texts [1,2]. The most recent review article in this field by Kirsh

[16] unfortunately, omitted some of the important works [17–28] published from mid-eighties to early ninties. In the present review article, we concentrate our attention on the analysis of TL based on the equations developed by Randall and Wilkins [10], Garlick and Gibson [11] and Chen [29].

1.2. *Basic theory of TL :*

During irradiation of a sample by X-rays, γ-rays *etc*, electrons are excited from the valence band to the conduction band leaving holes in the valence band. Both electrons and holes move in the respective bands until either each finds a localised defect where they are trapped or they might recombine directly with a charge carrier resulting in the emission of light. The localised energy level below the bottom of the conduction band where electrons are trapped is known as the electron trap (Figure 1). Similarly, the localised energy level just above the top of valence band is known as hole trap as it can trap holes present in the valence band. From thermodynamic considerations [1], it can be shown that the mean time τ spent in the trap by an electron or a hole can be written as

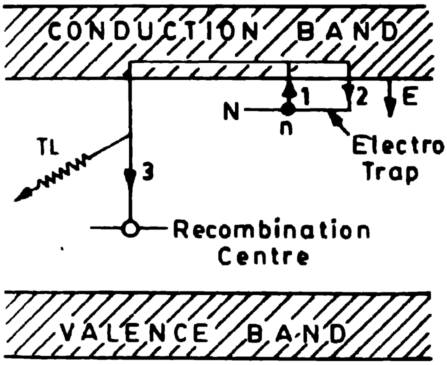

Figure 1. Schematic energy band model for TL. Steps 1, 2 and 3 are respectively the release of electron from the trap, retrapping of the electron and recombination of the electron and the hole.

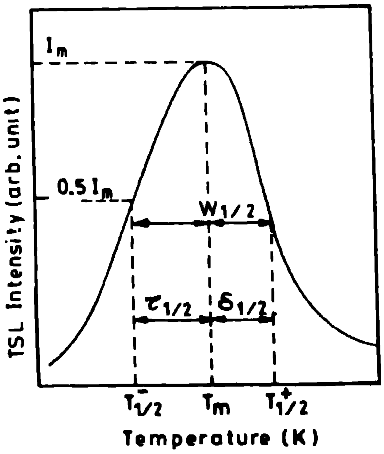

Figure 2. Schematic diagram of TL peak showing the relevant parameters at $x = 1/2$.

$$\tau = s^{-1} \exp (E/kT), \tag{1}$$

where k is the Boltzman constant and T is the temperature. During heating, a trapped electron will gain energy to escape from the trap and might recombine with a hole trap (which in this case acts as a recombination centre) resulting in the emision of light.

In the first order kinetics ($b = 1$) model of Randall and Wilkins [10], the possibility of retrapping is neglected. Thus, one can safely consider that the rate of recombination is equal to rate of release of the electrons from the traps. In this case, the TL intensity $I(t)$ as a function can be expressed as [10]

$$I(t) = -dn/dt = n\,s\ \exp(-E/kT), \tag{2}$$

where n is the density of trapped electrons. For a linear heating profile

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

where T_0 is the initial temperature, T is the temperature at time t and β is the linear heating rate. From eqs. (2) and (3) one can write

$$I(T) = n_0(s)\exp(-E/kT)\exp[(-s/\beta)\int_{T_n}^{T}\exp(-E/kT')dT']. \tag{4}$$

The TL intensity $I(T)$ is maximum at a temperature $T = T_m$ given by

$$\beta E/(kT_m^2) = s\exp(E/kT_m). \tag{5}$$

From eq. (5), it is seen that the peak temperature T_m depends on E, s and β. Garlick and Gibson [11] considered the effect of retrapping. Assuming equal probabilities of retrapping and recombination, they arrived at the equation

$$I(t) = -dn/dt = (n^2 s/N)\exp(-E/kT), \tag{6}$$

where N is the density of traps. Using eqs. (3) and (6) one gets

$$I(T) = (n_0^2 s/N)\exp(-E/kT)\left[1+(n_0 s/N\beta)\int_{T_0}^{T}\exp(-E/kT')dT'\right]^{-2} \tag{7}$$

In this case, the condition for maximum intensity is given by

$$1+(n_0 s/N\beta)\int_{T_0}^{T}\exp(-E/kT')dT' = [2n_0 skT_m^2/(N\beta E)]\ \exp(-E/kT). \tag{8}$$

From eq. (8), it is observed that unlike the first order case, T_m not only depends on E, s and β but also on the filling factor $f = n_0/N$. This point has been considered in details by Chen *et al* [30] and Gartia and Singh [31].

Chen [29] developed general order kinetics model of TL given by

$$I(t) = -dn/dt = s'n^b\exp(-E/kT) \qquad (\text{for } 0.7 \le b \le 2.5), \tag{9}$$

where $s = s'n_0^{b-1}$. According to a recent review article by Kirsh [16], eq. (9) is valid for $0.5 \le b \le 3.0$. From eqs. (3) and (9), we get for $b \neq 1$

$$I(T) = n_0 s\exp(-E/kT)[1+\{s(b-1)/\beta\}\int_{T_0}^{T}\exp(-E/kT')dT']^{-b/(b-1)}. \tag{10}$$

The condition for maximum intensity is given by

$$1+\{(b-1)s/\beta\}\int_{T_n}^{T}\exp(-E/kT')dT' = \{sbkT_m^2/\beta E\}\exp(-E/kT_m). \tag{11}$$

For $b = 2$ and $n_0 = N$ ($f = 1$), eqs. (10) and (11) reduce to (7) and (8) respectively. For $b = 1$, the expression for $I(T)$ is given by (4). Rasheedy [32] and independently Gartia *et al* [33] extended the validity for general order formalism for $f \neq 1$. According to them,

$$I(T) = Nf^b s\exp(-E/kT)\,[1+(b-1)f^b(s/\beta)$$

$$\int_{T_0}^{T}\exp(-E/kT')dT']^{-b/(b-1)} \qquad \text{for } b \neq 1, \tag{12}$$

and the maximum condition is given by

$$1+(b-1)f^{b-1}(s/\beta)\int_{T_0}^{T}\exp(E/kT')dT'$$

$$= \left(bsf^{b-1}\,kT_m^2/\beta E\right)\exp(-E/kT_m). \tag{13}$$

TL peaks represented by eq. (12) have been studied in details by Singh [34] and Ingotombi [35]. Such peaks show a shift in peak temperature with change of f. This has been observed experimentally by Gartia *et al* [36].

2. Symmetry factor and the order of kinetics

2.1. *Introductory remarks :*

The order of kinetics (b) of a TL process is very important as it can tell to some extent the physical process of charge trafficking mechanism inside the solid (section 1.2). The order of kinetics of a TL peak is manifested in its position, shape and intensity. The symmetry factor (μ_g) which is connected with the shape of the TL peak is used to determine the order of kinetics.

Halperin and Braner [37] were first to define the symmetry factor $\mu_g = \delta/\omega$, where δ is the half width towards the falling side of the TL peak and ω is the total width at half intensity such that $\omega = \tau + \delta$, τ being the half width towards the rising side of the TL peak. They [37] suggested that the first order kinetics is characterised by $\mu_g < e^{-1}$ (e is the base of natural logarithm) whereas $\mu_g > e^{-1}$ corresponds to the second order kinetics. Chen [29] observed that the symmetry factor depends strongly on b but weakly on E and s. He presented a curve connecting μ_g and b from which one can determine b by knowing μ_g. This method has been used by a number of TL workers with reasonable success [38–43].

Historically, the basis of the dependence of μ_g on b was first investigated by Fleming [44] who presented a table of temperatures corresponding to the fractional intensities $x = I/I_m$ (I_m is the peak intensity) for TL peaks with $b = 1$ and 2 for a range of activation energies $0.1 \leq E \leq 1.5$. It is to be noted that in general, experimental TL peaks are not isolated. Usually, there might be satellite TL peaks either on the rising side or on the falling side or on both the sides. In such a situation, it becomes difficult to determine the temperatures at half intensity. In order to overcome this, Gartia *et al* [45] introduced the method of the determination of symmetry factor not necessarily at half intensity points but at any fractional intensity points like $x = 1/5$, $1/2$, $2/3$ and $4/5$. Thus the symmetry factor μ_g at any fractional intensity can be defined (Figure 2) as

$$\mu_g(x) = (T_x^+ - T_m)/(T_x^+ - T_x^-) = \delta_x / \omega_x, \tag{14}$$

where T_x^- and T_x^+ are the temperatures corresponding to the fractional intensity x in the rising and falling sides of a TL peak. δ_x and ω_x represent half width at the falling side and full width for $I/I_m = x$. The effect of satellite peaks is less for higher values of x. Hence using the μ_g values corresponding to the higher values of x, one can estimate the order of kinetics even for a poorly isolated peak [45].

2.2. *Calculation of symmetry factor μ_g (x) for arbitrary values of b and x :*

Following Mazumdar *et al* [21] and Gartia *et al* [24] eqs. (4) and (5) for first order kinetics ($b = 1$) can be written in the form

$$I/I_m = \exp[u_m - u + F(u, u_m)], \tag{15}$$

where eqs. (10) and (11) for non-first-order kinetics ($b \neq 1$) can be expressed as

$$I/I_m = \exp(u_m - u)\,[1 - \{(b-1)/b\}F(u, u_m)]^{-b/(b-1)} \tag{16}$$

with

$$F(u, u_m) = u_m^2 \exp(u_m)\,[E_2(u_m)/u_m - E_2(u)/u], \tag{17}$$

where $E_2(u)$ is the second exponential integral [46], $u = E/kT$ and $u_m = E/kT_m$. Solving eqs (15) and (16) by an iterative method, one can determine $u_x^+ = E/kT_x^+$ and $u_x^- = E/kT_x^-$. From eq. (14), the symmetry factor is given by

$$\mu_g(x) = (u_m - u_x^+)u_x^- / (u_x^- - u_x^+)u_m. \tag{18}$$

2.3. *Determination of the order of kinetics from the symmetry factor :*

Gartia *et al* [24] have computed $\mu_g(x)$ for different values of x using eq. (18). They have found that for a particular value of x, $\mu_g(x)$ not only depends on b but also on u_m. In Figure 3, μ_g (1/2) is shown as a function of u_m for $b = 0.7$, 1.0, 1.5 and 2.5 for $10 \leq u_m \leq 100$. For experimentally observed TL peaks u_m belongs to this domain. We observe from Figure 3 that for a particular value of b, μ_g (1/2) decreases with increasing u_m. For $b = 1$, μ_g (1/2) varies from 0.446 to 0.408 as u_m changes from 10 to 100. For $b = 2$, the corresponding variation is from 0.547 to 0.506. In a similar way in Figure 4, we show the variation of μ_g (1/5) and μ_g (4/5) with u_m for $b = 1, 2$. Figure 5 shows the curve connecting μ_g (x) and x for different values of b corresponding to $u_m = 23$. Thus it is not possible to determine the order of kinetics uniquely unless u_m is known. Hence the comparison [47,48] of the value of b obtained from μ_g (1/2) using the method of Chen [29] with that of the isothermal decay method [1] is questionable. Table 1 shows the symmetry factor for different values of u_m to facilitate the preliminary estimation of the order of kinetics of an experimental TL peak.

An isolated second order TL curve (T_m = 320°C) of bluish green microcline ($KAlSi_3O_8$) a variety of potash feldspar was recorded [20,49] after thermally cleaning the lower temperature peaks upto 290°C (Figure 6a). This curve is ideal for testing the theoretical methods. The relevant temperatures required to evaluate μ_g (x) at $x = 1/2$, 2/3

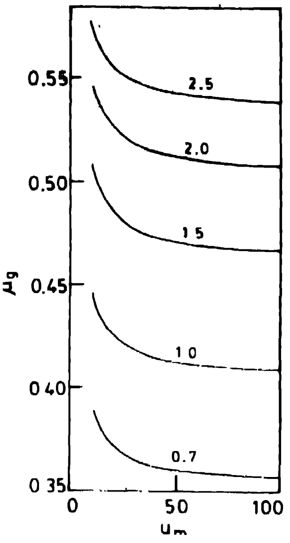

Figure 3. Variation of μ_g (1/2) with u_m for various orders of kinetics marked on the

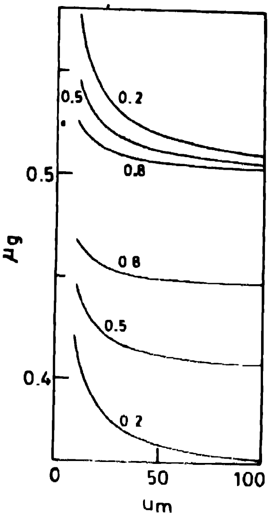

Figure 4. Variation of μ_g (x) with u_m for x = 1/2, 1/5 and 4/5. Upper set of three curves corresponds to $b = 2$ and the lower set for $b = 1$.

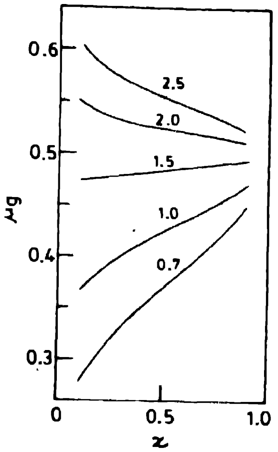

Figure 5. Variation of μ_g (x) with x for u_m = 23 for various orders of kinetics marked on the curves.

and 4/5 are given in Table 2. This table also contains the symmetry factor of a partly isolated peak at 203°C of X-irradiated Norwegian orthoclase (Figure 6b) recorded after thermal cleaning upto 107°C [45,49]. It is to be noted that μ_g (1/2) for 203°C peak is 0.557 which is rather higher than what is expected for a truely second order peak. This is due to the fact that the value of $T_{1/2}^{+}$ is affected by the presence of another peak with T_m = 280°C.

However, values of μ_g (2/3) and μ_g (4/5) are closer to those expected for second order kinetics. The peak can be best fitted to a second order TL curve with $E = 1.16$ eV and $s = 7.6 \times 10^{10}$ sec^{-1} demonstrating the suitablity of the present technique. Similarly, the peak shown in Figure (6a) can be fitted to a second order kinetics with $E = 1.42$ eV and $s = 3.56 \times 10^{10}$ s^{-1}.

Table 1. The values of μ_g (x) for some particular values of u_m and order of kinetics b.

	u_m	μ_g (1/5)	μ_g (1/2)	μ_g (4/5)
0.7	20	0.311	0.372	0.426
	30	0.302	0.365	0.422
	40	0.297	0.362	0.420
1.0	20	0.389	0.426	0.458
	30	0.378	0.418	0.453
	40	0.372	0 415	0.451
1.5	20	0 481	0 485	0.491
	30	0.468	0 477	0.487
	40	0.461	0.473	0.485
2.0	20	0 544	0.526	0.514
	30	0.531	0 518	0.510
	40	0 524	0.514	0.508
2.5	20	0 592	0.577	0.531
	30	0.579	0 549	0 527
	40	0.572	0.545	0.525

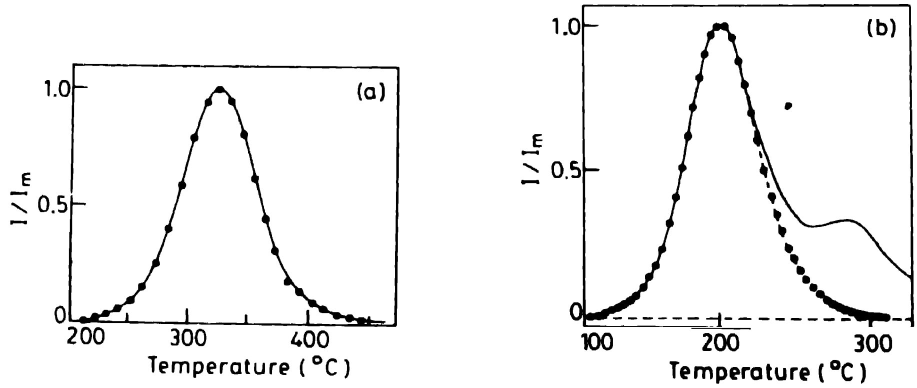

Figure 6. Curve fitting experimental glow peaks (a) completely isolated 320°C peak of bluish-green microcline and (b) partly isolated 203°C peak of X-ray irradiated (4 min) Norwegian orthoclase peak. The continuous curve denote experimental curve and symbols denote the second order fitted curve

2.4. *Determination of the order of kinetics using the point of inflection method :*

Following Land [50], Gartia *et al* [51] have shown that fractional intensity ratios I_{i1}/I_m and I_{i2}/I_m depend on u_m and b. Here I_{i1} and I_{i2} are the intensities at the temperatures T_{i1} and T_{i2}

Table 2. Symmetry factors of some experimentally observed TL peaks.

T_m (°C)	μ_g (1/2)	μ_g (2/3)	μ_g (4/5)
320	0.521	0.519	0.512
203	0.557	0.523	0.514

corresponding to the inflection points of a TL curve (Figures 7 and 8). It is to be noted that at these temperatures, the second derivative of TL glow curve with respect to temperature vanishes. The fractional intensity ratios are strongly dependent on b. In Figure 9 we show these dependences for u_m = 23, which can be used to estimate the order of kinetics.

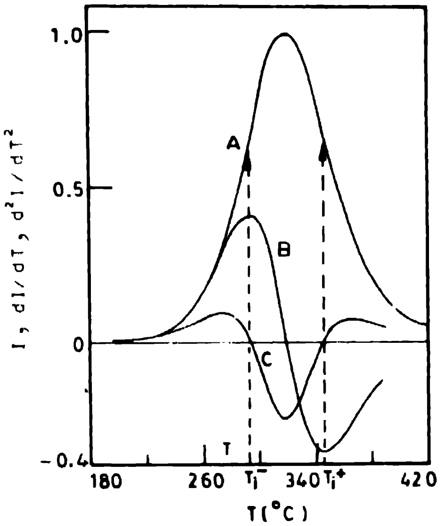

Figure 7. Isolated 320°C peak in bluish-green microcline ($KAlSi_3O_8$) obtained by thermally cleaning the low temperature peaks by heating upto 290°C. A : TL curve; B and C are respectively stand for first and second derivatives of the TL curve with respect to temperature.

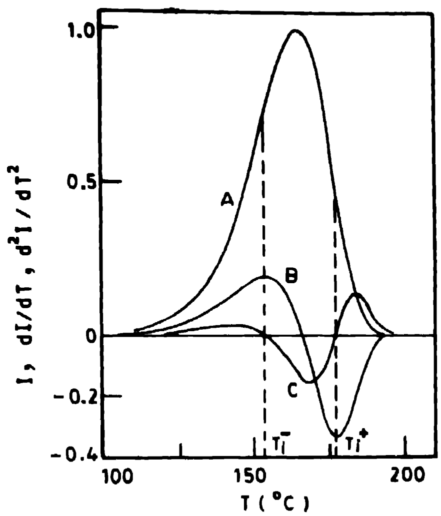

Figure 8. Same as Figure 7 but for isolated 165.5°C peak in Ca doped KCl.

3. Determination of the activation energy of a TL peak by using the peak shape and points of inflection methods

3.1. *Peak shape method :*

Of the various methods used for the determination of the activation energy of a TL peak, the methods based on its shape is popularly known as peak shape methods. These methods have been reviewed in details by Kirsh [16], McKeever [2] and Chen and Kirsh [1]. Peak shape methods require the prior knowledge of the order of kinetics. The conventional peak shape methods use only the temperatures at half intensity points. Christodoulides [18], Mazumdar *et al* [21] and Gartia *et al* [25] extended these methods for an arbitrary value of fractional intensity x.

From eqs. (15) and (16), it can be shown [18,21,25] that to a very good approximation, a linear relation exists between the following pairs of variables

$$\left[u_m, u_x^-/(u_x^- - u_m)\right], \left[u_m, u_x^+/(u_m - u_x^+)\right] \text{ and } \left[u_x^-, u_x^+/(u_x^- - u_x^+)\right]$$

so that one can write

$$E_1 = \frac{A_1 kT_m^2}{(T_m - T_x^-)} + B_1 kT_m, \tag{19}$$

$$E_2 = \frac{A_2 kT_m^2}{(T_x^+ - T_m)} + B_2 kT_m \tag{20}$$

and

$$E_3 = \frac{A_3 kT_m^2}{(T_x^+ - T_x^-)} + B_3 kT_m. \tag{21}$$

By using the method of non-linear least square regression, each of the coefficients A_j and B_j (j = 1 – 3) can be expressed as a quadratic function of b ($0.7 \le b \le 2.5$) as [25]

$$A_j = c_{0j} + c_{1j} b + c_{2j} b^2 \tag{22}$$

and

$$B_j = d_{0j} + d_{1j} b + d_{2j} b^2. \tag{23}$$

Table 3. The coefficients c_{ij} and d_{ij} for calculating A_j and B_j in the peak shape method.

x	j	c_{0j}	c_{1j}	c_{2j}	d_{0j}	d_{1j}	d_{2j}
1/2	1	1 019	0.504	– 0.066	– 1.059	– 1.217	0.109
	2	0.105	0.926	– 0.048	0 154	– 0.205	– 0.128
	3	1.124	1.427	– 0.113	– 0.902	– 0.346	– 0.061
2/3	1	0.684	0.426	– 0.055	– 0.720	– 1.210	0.098
	2	0.146	0.683	– 0.048	0.184	– 0.432	– 0.094
	3	0.830	1.108	– 0 103	– 0.529	– 0.607	– 0.029
4/5	1	0.449	0.342	– 0.043	– 0.480	– 1.184	0.085
	2	0.153	0.487	– 0.041	0.180	– 0.606	– 0.062
	3	0.602	0.829	– 0.084	– 0.293	– 0.777	– 0.006

The values of c_{ij} and d_{ij} are tabulated in Table 3. In this context, we would like to mention that Christodoulides [18] and Mazumdar *et al* [21] reported the values of A_j and B_j for b = 1, 1.5 and 2. Expressions (19)–(21) are applied to some numerically computed TL peaks and the results are compared with those of Chen [1,29] in Table 4. From this table, we see that the present results are in better agreement with the input values E_{in} of the activation energy than those of Chen [29].

Table 4. Comparison of the values of activation energies E_1, E_2 and E_3 calculated in the peak shape method with E_τ, E_δ and E_ω of Chen [29] for some computer generated TL peaks.

E_{in} (eV)	b	$T_m(K)$	E_1 (eV)	E_τ (eV)	E_2 (eV)	E_δ (eV)	E_3 (eV)	E_ω (eV)
1.6	2.5	554.1	1.594	1.583	1.599	1.486	1.598	1.535
1.6	1.9	554.6	1.603	1.599	1.602	1.575	1.603	1.595
1.6	1.5	554.9	1.600	1.606	1.599	1.616	1.600	1.623
1.6	1.1	555.2	1.594	1.605	1.597	1.591	1.596	1.613

Expressions (19)–(21) have been applied to compute the activation energies of a number of experimental TL peaks *viz.* (i) 165.5°C TL peak (Figure 8) of Ca doped KCl, X-irradiated at room temperature followed by thermal cleaning up to 150°C [21], (ii) isolated 320°C peak (Figure (6a)) of bluish green microcline [20,49], (iii) glow curve (Figure 10) of tremolite γ-irradiated (dose = 1.7×10^5 Gy) [52], (iv) third peak (Figure 11) of tremolite obtained by thermal cleaning of first and second peaks, (v) first peak (Figure 12) of actinolite [52] and (vi) TSL peaks of CdS : S and CdS : A samples recorded by Lee *et al* [53]. The values of E_1, E_2 and E_3 for these peaks are tabulated in Table 5. There is a good agreement among these activation energies and for cases (i) and (ii), the values also agree with the corresponding curve fitting values E_{cf} of the activation energy *viz.* 1.36 eV and 1.42 eV, which advocates the suitability of the expressions (19)–(21). Singh *et al* [54]

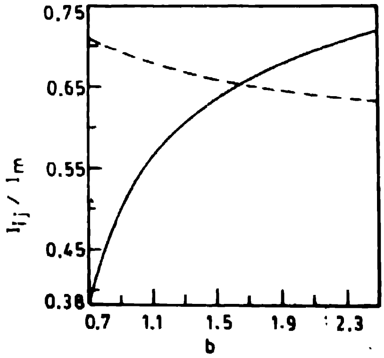

Figure 9. Variation of I_{i1}/I_m and I_{i2}/I_m with b for $u_m = 23$. Solid curve corresponds to $j = 2$ and broken curve corresponds to $j = 1$.

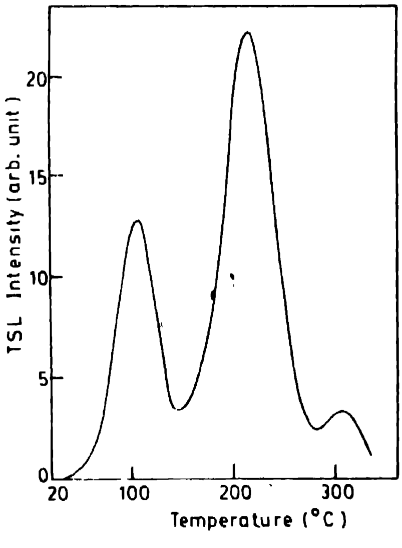

Figure 10. Glow curve of γ-irradiated tremolite.

and Singh [55] suggested a varient of peak shape method which does not require the prior knowledge of the order of kinetics.

Table 5. Activation energies of some experimental TL peaks by using the peak shape method.

Material	$T_m (K)$	b	x	E_1 (eV)	E_2 (eV)	E_3 (eV)
KCl : Ca	438.5	1	1/2	1.34	1.37	1.34
			2/3	1.34	1.33	1.36
			4/5	1.42	1.37	1.41
$KAlSi_3O_8$	593	2	1/2	1.37	1.37	1.37
			2/3	1.39	1.37	1.38
			4/5	1.33	1.32	1.32
Tremolite	377	2	1/2	0.84	0.92	0.99
			2/3	0.81	0.86	0.84
			4/5	0.82	0.80	0.81
Tremolite	487	2	1/2	1.11	1.13	1.12
			2/3	1.11	1.30	1.12
			4/5	1.12	1.11	1.11
Tremolite	573	1	1/2	1.37	1.46	1.40
			2/3	1.37	1.51	1.43
			4/5	1.43	1.59	1.50
Actinolote	369	2	1/2	0.70	0.72	0.71
			2/3	0.65	0.67	0.66
			4/5	0.63	0.67	0.65
CdS : S	190	1	1/2	0.26	0.28	0.27
			2/3	0.26	0.27	0.27
			4/5	0.28	0.26	0.27
CdS : A	295	1.5	1/2	0.83	0.82	0.82
			2/3	0.84	0.82	0.83
			4/5	0.81	0.79	0.80
CdS : S	320	1	1/2	0.50	0.53	0.51
			2/3	0.50	0.53	0.51
			4/5	0.52	0.56	0.53

3.2. Point of inflection method :

In this method, activation energy is determined by using the temperatures T_{i1} and T_{i2} corresponding to the points of inflection of a TL peak. It has been shown by Singh *et al* [56] that one can get expressions of the type (19)–(21) with T_x^- and T_x^+ replaced by T_{i1} and T_{i2} respectively. The corresponding coefficients c_{jk} and d_{jk} are presented in Table 6. Singh *et al*

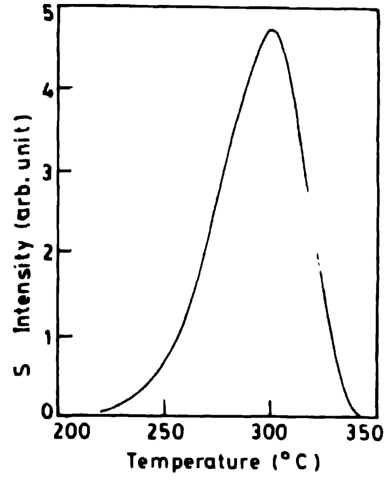

Figure 11. Third TL peak of tremolite obtained by thermal cleaning of first and second peaks.

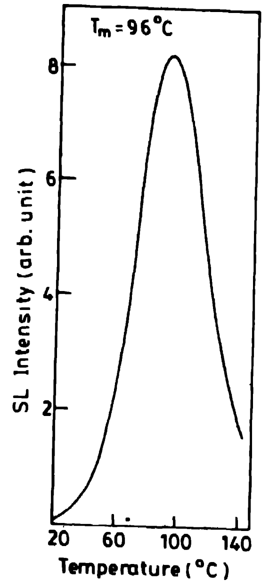

Figure 12. First peak of actinolite.

Table 6. The coefficients c_{jk} and d_{jk} for calculating A_j and B_j in the point of inflection method.

k	c_{0k}	c_{1k}	c_{2k}	d_{0k}	d_{1k}	d_{2k}
1	0 873	- 1.562	0.133	0.449	0.585	- 0.075
2	0 668	- 1.849	0.150	0.448	0.587	- 0.076
3	0.939	- 1 706	0.142	0.897	1.172	- 0.151

Table 7. Activation energies of some computer generated TL peaks computed by point of inflection method.

b	$T_m(K)$	E_{in}(eV)	E_1 (eV)	E_2 (eV)	E_3 (eV)
2.5	554.1	1.60	1.59	1.60	1.59
1 9	554.6	1.60	1.60	1.61	1.60
1.5	554.9	1.60	1.59	1 60	1.60
1.1	555.2	1.60	1.60	1.59	1.59

[56] computed the values of E_1, E_2 and E_3 of some computer generated and experimental TL peaks (Figures 7 and 8) and obtained excellent results (Tables 7 and 8).

Table 8. Values of E_1, E_2, E_3 calculated by using eqs. [19–21] and coefficients given in Table 6 for experimental TL peaks [20,21,56].

T_m (*K*)	*b*	E_{cf}(eV)	E_1 (eV)	E_2 (eV)	E_3 (eV)
593	2	1.42	1.43	1.42	1.43
438.5	1	1.36	1.35	1.36	1.35

4. Determination of the activation energy by the initial rise (IR) and various heating rates (VHR) methods

Methods for the determination of the activation energy discussed in the earlier section require the prior knowledge of the order of kinetics. In some cases, it is very difficult to have the prior knowledge of the order of kinetics. IR and VHR methods can be used to determine the activation energy even if the order of kinetics is not known. In the present section, we estimate the systematic errors in these two methods.

4.1. VHR method :

Methods of various heating rates as a means of determining trap depths *E* for TL measurements have been widely used. These methods are based on repeated measurements of a certain peaks at different heating rates keeping all other parameters constant. One advantage of these methods is that only properties related to the maximum point itself *viz.* T_m and/or I_m are to be measured. The use of two heating rates for the evaluation of *E* was suggested by Booth [57]. Hoogenstraaten [58] suggested the use of several heating rates and according to his method, a plot of ln (T_m^2 / β) *versus* $1/T_m$ should yield a straight line of slope E/k. Chen and Winer [59] suggested a method in which a plot of ln (I_m) *versus* $1/T_m$ gives a straight line with slope E/k. Singh *et al* [27] and Gartia *et al* [28] estimated the errors involved in the determination of the activation energy by various heating rates methods of Hoogenstraaten [58]. Chen and Winer [59] and two heating rates method of Booth [57].

According to Booth [57] method

$$E_B = \frac{kT_{m1}T_{m2}}{T_{m1} - T_{m2}} \ln\left[\left(T_{m2}^2 / \beta_2\right)\left(\beta_1 / T_{m1}^2\right)\right], \tag{24}$$

where E_B is the activation energy determined by the Booth method, T_{m1} and T_{m2} are the peak temperatures corresponding to the linear heating rates β_1 and β_2. Eq. (24) is strictly valid for $b = 1$. Gartia *et al* [28] computed the percentile proportional error $\delta_B = [(E_B - E)/E] \times 100\%$ in the determination of activation energy by Booth method. *E* is the input value of the activation energy. They found that for $b \neq 1$, E_B is always greater than *E i.e.* Booth method overestimates the activation energy. The plot of δ_B as a function

b ($1.1 \leq b \leq 2.5$) for $E = 1$ eV and $s = 10^{12}$ sec^{-1} is shown in Figure 13. δ_B almost increases linearly with b. It is also found that for a particular value of b, δ_B decreases with increasing s. δ_B is nearly insensitive to the input value of E. The maximum value of δ_B is less than 1% for non-first-order of kinetics. Hence, Gartia *et al* [28] concluded that it is applicable for non-first-order kinetics in accordance with the observations made by Chen and Kirsh [1]. Gartia *et al* [28] also suggested another version of two heating rates method according to which the activation energy E_G is given by

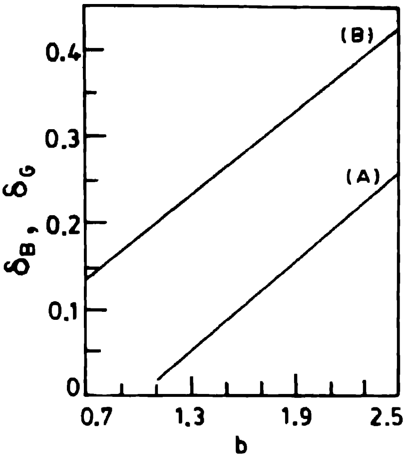

Figure 13. Systematic errors δ_B (curve A) and δ_G (curve B) as a function of b.

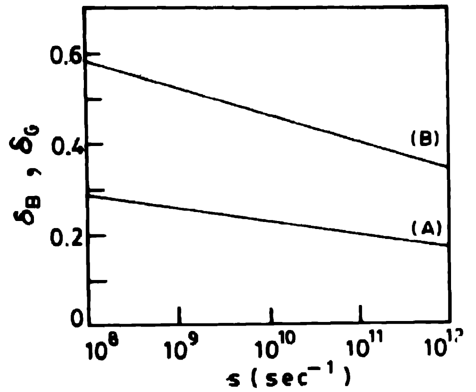

Figure 14. δ_B (curve A) and δ_G (curve B) as function of s for $b = 2$

$$E_G = \frac{kT_{m1}T_{m2}}{T_{m1} - T_{m2}} \ln\left[I_{m1} / I_{m2}\right], \tag{25}$$

where I_{m1} and I_{m2} are the peak intensities. The percentile proportional error involved in this method is denoted by δ_G. The variation of δ_G as a function of b for $s = 10^{12}$ sec^{-1} is shown in Figure 13. The variation of δ_G with s for $b = 2$ is shown in Figure 14.

Table 9. Activation energies E_B and E_G for some numerically computed TL peaks.

E_{in} (eV)	b	s (sec^{-1})	E_B (eV)	E_G (eV)
1.0	2.0	10^8	1.003	1.006
		10^9	1.003	1.005
		10^{10}	1.002	1.004
		10^{11}	1.002	1.004
		10^{12}	1.002	1.003

This method like the Booth method overestimates the value of E. In Table 9 we present the activation energies E_B and E_G for second order TL peaks corresponding to the different values of s. It is found that E_B and E_G are identical for all practical purposes.

TL curves of γ-irradiated limestone (thermally cleaned upto 170°C to remove a lower temperature peak) recorded with two values of heating rates are presented Figure 15. The glow curve exhibits a fairly isolated peak in the region of 220–240°C followed by another peak occurring in the form of a shoulder. The symmetry factor μ_g (1/2) of the 220–240°C peak is found to be close to 0.52 indicating second order kinetics [24]. The values of E_B and E_G for this peak come out to be 1.43 eV and 1.45 eV respectively, whereas the values of the activation energies of the same peak analyses by the initial rise method [11] and Hoogenstraaten method [58] are 1.52 eV [60]. It shows that the Booth method [57] and the method proposed by Gartia *et al* [28] can be used for TL peaks of any order of kinetics for all practical purposes.

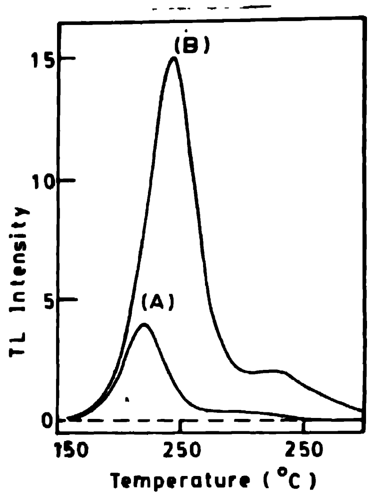

Figure 15. TL curves of γ-irradiated (1.8×10^3 Gy) limestone for two different heating rates, 50°C/min (curve A) and 200°C/min (curve B). The first peak is thermally cleaned.

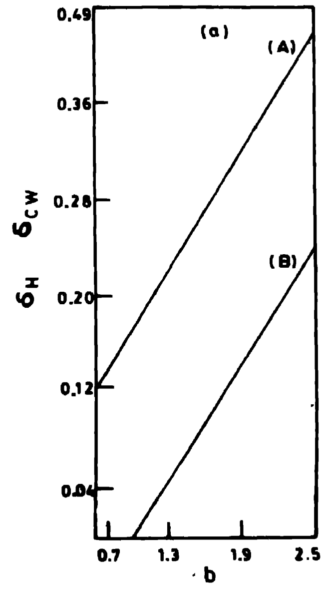

Figure 16. Errors δ_H (curve B) and δ_{CW} (curve A) in the determination of the activation energy as a function of b.

Singh *et al* [27] computed the percentile proportional errors δ_H and δ_{CW} in the determination of the activation energy by the Hoogenstraaten method [58] and the method of Chen and Winer [59]. Figures 16 and 17 show the variations of δ_H and δ_{CW} with b and s respectively for $E = 1$ eV. These errors are found to be independent of E. Hoogenstraaten method [58] is accurate for $b = 1$. The errors are almost linear and increasing functions of b. On the other hand, they decrease with s. It has also been noted that the maximum error in both the methods are about 1% and they overestimate the value of E. Hence, even if the order of kinetics is unknown in a TL process, these methods [58,59] can be used for the determination of the activation energy.

4.2. *Initial rise method :*

The initial rise (IR) method suggested by Garlick and Gibson [11] is based on the assumption that for $T \ll T_m$ and $I \ll I_m$, the TL intensity can be written as I = Cons. exp $(-E/kT)$ so that a plot of ln (I) against $1/T$ results in a straight line with slope E/k. This method is very much popular due to a number of reasons : (i) it does not require the prior knowledge of b and T_m, (ii) only small portion of the TL curve is used. However, in this method there is a systematic error as a result of which, it always underestimates the activation energy. In Figure 18 we plot the error $\delta_{IR} = [(E - E_{IR})/E] \times 100\%$, ($E_{IR}$ is the activation energy determined by the IR method) as a function of b for $s = 10^{12}$ sec^{-1} and E = 1 eV. There is a common belief that the errors of the IR method do not depend on b which is in contradiction to our observation from Figure 18, a point already noted by Singh *et al* [22]. We have studied two cases using (i) 10% (curve A, Figure 18) and (ii) 15% (curve B, Figure 18) of the initial rise portion of the glow curve. It is seen that the error is larger in case (ii) than in case (i). Christodoulides [19] and Singh *et al* [22] suggested a method to correct the systematic error when both the order of kinetics and peak temperature is known.

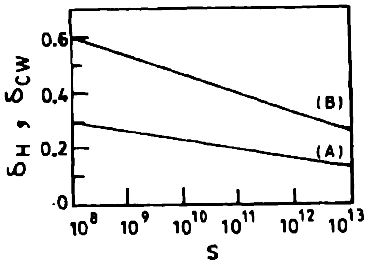

Figure 17. δ_H (curve A) and δ_{CW} (curve B) as a function of the frequency factor s

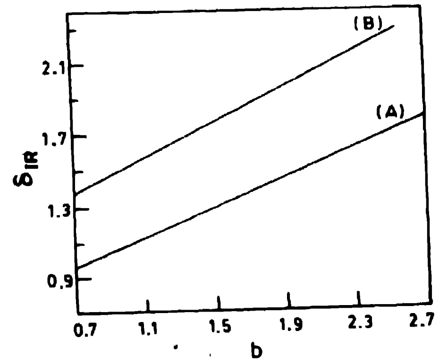

Figure 18. Error δ_{IR} in the determination of E as a function of b by the initial rise method. Curve A used only 10% of the initial rise portion of the glow curve, curve B only 15%.

4.3. *Curve fitting method :*

In the curve fitting method, one attempts to match an experimental TL curve with numerically computed first and general order TL equations (Section 1.4) by using a suitable minimization procedure [1,16,60]. In this method, one can extract trapping parameters E, s and b for an experimental TL peak. This procedure is indispensible when the glow curve contains a number of peaks. The technique has attained rather a high degree of sophistication and various groups have successfully utilised it [17,21,23,26,36,45,61–64].

5. Temperature dependence of the frequency factor

So far, we have assumed that frequency factor does not depend on temperature. But as shown by Keating [65], Aramu *et al* [66], Saunders [67], Kivits and Hagebeuk [14], Chen and Kirsh [1] and Fleming [68], the frequency factor s can be expressed as $s = s_0T^a$ with $-2 \le a \le 2$. Under this condition, (4) and (10) become

$$I(T) = n_0 s_0 T^a \exp(-E/kT)\exp[-(s_0/\beta)\int_{T_0}^{T} T'^a \exp(E/kT')dT'] \quad (26)$$
$$\text{for } b = 1$$

and

$$I(T) = s_0 n_0 T^a \exp(-E/kT)[1 + s_0(b-1)/\beta\int_{T_0}^{T} T'^a \exp(-E/kT')dT']^{-b/(b-1)}. \quad (27)$$
$$\text{for } b \neq 1$$

The corresponding maximum conditions are

$$(E/kT_m^2) - (s_0T_m^a/\beta)\exp(-E/kT_m) + a/T_m = 0 \quad (28)$$

and

$$\left[\frac{a}{T_m} + \frac{E}{kT_m^2}\right][1 + \{s_0(b-1)/\beta\}\int_{T_0}^{T} T'^a \exp(-E/kT')dT'] = (bs_0T_m^2/\beta)\exp(-E/kT_m), \quad (29)$$

and the analogous of (15)–(17) are given by

$$I/I_m = (u_m/u)^a[\exp(u_m - u) + F(u,u_m)] \quad \text{for } b = 1 \quad (30)$$

and

$$I/I_m = (u_m/u)^a[1 - \{(b-1)/b\}F(u,u_m)]^{-b/(b-1)} \times \exp(u_m - u) \quad (31)$$
$$\text{for } b \neq 1,$$

with

$$F(u,u_m) = (u_m^2 + au_m)u_m^a \exp(u_m)\,[E_{a+2}(u_m)/u_m^{a+1} - E_{a+2}(u)/u^{a+1}], \quad (32)$$

where $E_m(u)$ is the m-th order exponential integral.

Using eqs. (26)–(29), Gartia *et al* [69] computed the errors δ_{IR}, δ_H and δ_{CW}. For $a > 0$ both the IR and VHR methods overestimate E whereas for $a < 0$, they underestimate it. Gartia *et al* [69] concluded that even if the frequency factor is temperature-dependent, these methods can be used irrespective of the order of kinetics. The absolute magnitude of the errors incurred in the activation energy is about an order of magnitude larger than the case of the temperature-independent frequency factor. Singh *et al* [70] examined the validity of peak shape method in this case. They found that the dependence of $\mu_g\,(x)$ on a is very weak, which makes it difficult to estimate a from an experimental TL peak. They also showed that in this case, the peak shape method of Gartia *et al* [25] can lead to a maximum error of 10% in the determination of the activation energy.

6. Summary and conclusions

The recent developments on the analysis of TL can be summarised as follows.

(i) The three parameter formalism of TL inspite of its criticism is a practical approach to estimate lifetime of a charge carrier in a trap which in turn, is the single dominant parameter that determines the range of dating limit.

(ii) The order of kinetics can be easily estimated from the shape factor of a glow peak. The shape factor need not be determined solely at the fractional intensity $x = 1/2$. It may be determined at any other suitable fractional intensity ($x = 2/3$ or $4/5$) depending upon the level of contamination by the satellite peaks. However for final confirmation, one has to use the curve fitting method.

(iii) The order of kinetics can also be determined using the points of inflection.

(iv) At the present state of development, one need not have a very well isolated glow peak to determine the activation energy by using peak shape methods since there exist formulae which essentially use only two points of a glow peak.

(v) The maximum error that can occur in the determination of activation energy by IR method is about 2% and 3% when one uses 10% and 15% of the glow curve maximum. Hence for practical purposes, activation energy of any curve can be determined using IR method irrespective of the order of kinetics. Using corrected IR method, this can be further minimised.

(vi) E can be determined by using the VHR method which can also be used irrespective of the order of kinetics. Even the two heating rates methods are good enough.

(vii) Curve fitting method is another powerful technique to determine the activation energies of a complex glow curve. With the availability of the standard routines and personal computers this method should not pose any difficulty.

(viii) The temperature dependence of frequency factor which has often perplexed TL workers need not be taken seriously. In this case also, one can safely use peak shape, IR and VHR methods as far as practical determination of lifetime of charge carriers in a trap is of primary consideration.

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