The Effect of Temperature Dependent Frequency Factor on the Evaluated Trapping Parameters of TSL Glow Curves

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Abstract

The effect of temperature dependency on frequency factor and its relationship to trapping parameters is discussed by using the peak shape method. The coefficients appearing in the peak shape formula for the calculation of the activation energy have been determined and tabulated for the symmetry factor $\mu_g(X)$ for $x = 0.50$ and 0.75 of the peak intensity. It is found that significant errors occur in the value of the trapping parameters if the temperature dependecy of the frequency factor is not consider.

1. Introduction

The various experimental techniques have been developed to determine the trapping parameters of any trap in a crystal from the thermally stimulated luminescence (TSL) peaks. Some of them are the initial rise (IR), variable heating rate (VHR); isothermal decay and peak shape method among others [1].

The peak shape method is one of the most utilized technique to determine trapping parameters, namely, the thermal activation energy E, the frequency factor s and the kinetic order b.

Many expressions have been proposed over the last forty years based on the shape of the glow curves for the determination of the activation energy [2]. Recently, Mazumdar et al. [3] and Christodulies [4] proposed some simple expressions for the determination of the activation energy based on the shape of the glow curve. However, almost all of these expressions are developed on the assumption that the frequency factor is temperature independent. But it has been shown that this assumption results in a significant error in the value of the activation energy [5-7].

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The subject of the temperature dependent frequency factor, which arises from the temperature dependence of the electron trap capture cross section σ with $T^x(-4 \leq x \leq 0)$, the mean thermal velocity of a free electron ν with $T^{1/2}$ and the effective density of states in the conduction band N_c with $T^{3/2}$ was first examined by Keating, who proposed a formula for the calculation of the activation energy [8]. But Chen showed that Keating's formula had some limitation and accuracy problems and thus he developed his own expressions based on the temperature dependent frequency factor for the calculation of E By using a various combination of theoretical and computation of theoretical and computational analysis [9]. Lately, Fleming [5] and Gartia at el. [6] woked on the determination of activation energy by considering the temperature dependent frequency factor in their calculation. They come to a conclusion that there would be an error of about an order of $\pm$ 10% if the temperature frequency dependency factor is not considered. S. D. Singh et al. [7] evaluated the coefficients C_α and D_α appearing in the peak shape formula for the calculation of the activation energy only for the symmetry factor $\mu_g(x)$ at x=0.50.

In the present work we investigated the effect of temperature dependent frequency factor on the symmetry factor (μ_g) and activation energy E by using the peak shape method. We also evaluated the coefficients $C_{\alpha x}$ and $D_{\alpha x}$ for the symmetry factor $\mu_g(x)$ at x=0.50 and 0.75 for the general order kinetics.

2. Theory

2.1. First Order Kinetic (b=1)

Following Fleming [5] and Singh et al.[7] the glow intensity at any time t for a temperature, dependent frequency factor is given by

$$I(t) = -C\frac{dn(t)}{dt} = -n(t)_{S_0}T^a \exp(-\frac{E}{kT}), \tag{1}$$

and integrating with respect to temperature, we have

$$I(T) = Cn_{0S_0}T^a \exp(-\frac{E}{kT} - \frac{S_0}{\beta}\int_{T_0}^{T} T'^a \exp[-\frac{E}{kT'}]dT'). \tag{2}$$

In the equation 2, all the symbols have the usual meaning and the temperature dependent frequency factor is expressed as $S = S_0T^a$ with $-2 \leq a \leq 2$.

At the peak temperature T_m, the derivative of equation (2) with respect to T becomes

$$\frac{E}{kT_m^2} - S_0T_m^a\frac{\exp[-\frac{E}{kT_m}]}{\beta} + \frac{a}{T_m} = 0. \tag{3}$$

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2.2. Non-First order Kinetics $(b \neq 1)$

Following Fleming [5] we have

$$I(t) = -C\frac{dn(t)}{dt} = n^b(t)S_0'T^a \exp(-\frac{E}{kT}) \qquad (4)$$

and integrating with respect to T we obtain

$$I(T) = Cn_0^b S_0' T^a \exp[-\frac{E}{kT}](1 + [S_0' n_0^{b-1}\frac{(b-1)}{\beta}]\int_{T_0}^{T} T'^a \exp[-\frac{E}{kT'}]dT')^{-\frac{b}{(b-1)}}, \qquad (5)$$

where S_0 in equation (1) is replaced by S_0' in equation (4) to reflect a change in dimension.

At the peak temperature T_m, the derivative of equation (5) with respect to T becomes

$$\frac{a}{T_m} + \frac{E}{kT_m} = bS_0' n_0^{b-1}T_m^a \frac{\exp[-\frac{E}{kT_m}]}{\beta}(1 + [S_0' n_0^{b-1}\frac{b-1}{\beta}]\int_{T_0}^{T_m} T'^a \exp[-\frac{E}{kT'}]dT'). \quad (6)$$

The temperature dependent frequency constant S_0 can be calculated from the equation (3) and equation (6) for first-order and non-first order kinetics for given values of E, a, b, b and T_m.

The integral occurring in equations (2), (5), (6) can not be evaluated exactly. The follolwing procedure is used in the evaluation of integral. Let

$$J(T) = \int_{T_0}^{T} T^a \exp[-\frac{E}{kT}]dT \qquad (7)$$

with $u = E/kT$; equation [7] can be written as

$$J(u) = (\frac{E}{k})^{1+a}\int_{v}^{v_0} U^{-(a+2)}\exp(-u)du \qquad (8)$$

which can be expressed in terms of the incomplete gamma function as

$$J(u) = \left(\frac{E}{K}\right)^{1+a}[\Gamma(-1-a, u) - \Gamma(-1-a, u_0)]. \qquad (9)$$

The incomplete gamma function can only be solved for integer and half-integer values of a. For positive and negative integer values of a except a=-2, the evaluation of equation (9) involves the Exponential Integral $E_i(u)$. For positive and negative half-integer of the values of a, the equation (9) can be evaluated by means of Error Function Erf(u) [7,10].

Following Singh et al. [11], $U_m = E/kT_m$ can be expressed as linear function of $U_{x1}U_{x2}/U_m(U_{x1} - U_{x2})$ for $T_{x1} < T_{x2}$, where T_{x2} are the temperatures in the rising and falling sides at the intensity ratio x, $U_{x1} = E/kT_{x1}$ and $U_{x2} = E/kT_{x2}$, so we can write

$$E = C_{\alpha x}\frac{kT_m^2}{T_{x_2}T_{x_1}} + D_{\alpha x}kT_m, \qquad (10)$$

where $T_{x2} - T_{x1} = \tau_x, \delta_x, \omega_x$ and $\alpha = \tau, \delta, \omega$.

In our numerical calculation of $C_{\alpha x}$ and $D_{\alpha x}$, it was seen that not only $D_{\alpha x}$ depends on a but also $C_{\alpha x}$ depends on a and they can be expressed as

$$
\begin{aligned}
C_{\alpha x} &= C_{0x} + C_{1x}a \\
D_{\alpha x} &= D_{0x} + D_{1x}a
\end{aligned}
\qquad (11)
$$

The symmetry factor is defined in [7]

$$\mu_g(x) = \frac{u_{x_1}(u_m - u_{x_2})}{U_m(U_{x_1} - U_{x_2})}. \qquad (12)$$

The T_{x1} and T_{x2} can be found by solving the equation (2) and equation (5) at x=0.50 and 0.75. As mentioned before, S. D. Singh et al. evaluated the coefficients $C_{\alpha x}$ and $D_{\alpha x}$ at the half-intensity (x=0.50). However this data is only good for the determination of the activation energy of the isolated glow peaks [12]. But, for poorly and partly isolated glow peaks one can not use their data. Therefore, we have determined the coefficients $C_{\alpha x}$ and $D_{\alpha x}$ not only at the half-intensity x=0.50 but also at x=0.75 of the maximum intensity. So that one can use our data to calculate the activation energy of any glow peaks.

3. Desult and Discussion

In the previous section, following Fleming [5] and Sing et al. [6] procedures are outlined and expressions are presented to evaluate the activation energy, frequency factor and geometric shape factor. First we calculated the shape factor $\mu_g(x)$ at x=0.75 as a function of U_m. Figure 1a and 1b shows the variation of $\mu_g(x)$ as a function of U_m for $10 \leq U_m \leq 100$ and $-2 \leq a \leq 2$ for two values of kinetic order b namely 1 and 2. The varitaion of $\mu_g(x)$ with U_m is similar in two figures but the magnitude is different. Another point is that the curves corresponding to different values of a almost merge for $U_m \geq 20$ and that there are no meaningful difference between different values of a for $U_m \geq 20$. This finding agrees with the results of Fleming and Singh et al. Since U_m is greater than 20 for the most TLD materials, we conclude that the dependence of $\mu_g(x)$ on U_m is very weak.

The shape factor $\mu_g(x)$ evaluated at x=0.50 and 0.75 is plotted against a in Figure 2a and 2b to show the explicit dependence of $\mu_g(x)$ on a, for $U_m = 10$ and b=0.7; 1.0;

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1.25; 1.5; 2.0 and 2.5. We see that as a changes from -2 to 2 $\mu_g(x)$ decreases by about 5% for all b values. However for $U_m > 20$, it is not almost possible to distinguish $\mu_g(x)$ against a for all b values. Hence $\mu_g(x)$ weakly dependens on a for high values of U_m above 20.
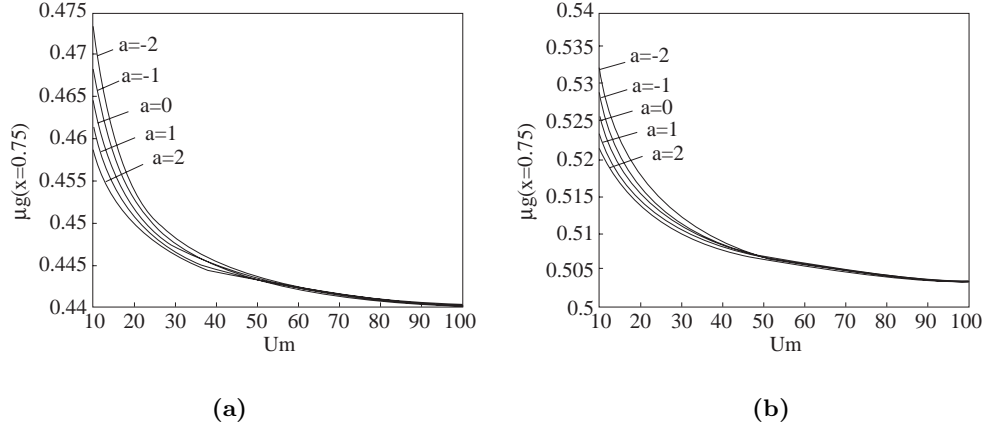

Figure 1. Variation of the shape factor $\mu_g(x)$ with U_m at x=0.75 (a) for the kinetic order b=1.0 and (b) for the kinetic order b=2.0
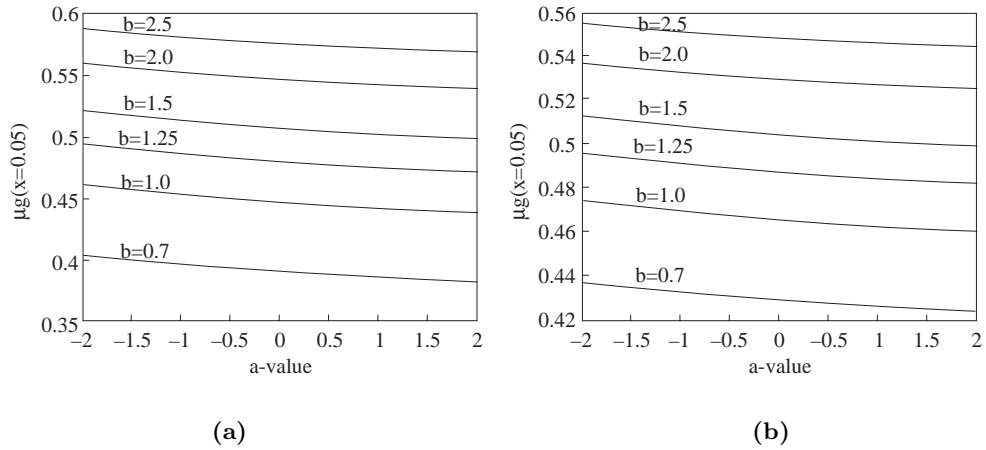
Figure 2. Variation of the shape factor $\mu_g(x)$ with a for the U_m =10 and b=0.7, 1.0, 1.25, 1.5, 2.0 2.5. (a) x=0.5 and (b) x=0.75

We have also calculated the activation energy of numerically computed TL peaks for $-2 \leq a \leq 2$ and b=1.0 at x=0.50 for $\alpha = \tau, \delta, \omega$. Then we determined the possible

error that occurs if one does not consider the temperature dependency of the frequency factor. Figure 3a, b and c show the percentage error in the activation energy as a function of U_m. The percentage error is defined as the difference between the activation energy of numerically computed TL peaks with $-2 \leq a \leq 2$ and with a=0. It is obvious that the activation energy calculated by not considering the temperature dependency of frequency factor can lead to an error as much as 20% at $U_m = 10$ and 10% at $U_m = 20$. This result is also in good agreement with the findings of Fleming [5] and Singh et al. [6]. The coefficients $C_{\alpha x}$ and $D_{\alpha x}(\alpha = \tau, \delta, \omega)$ for x=0.50 and 0.75 have been evaluated by using a numerical computer calculation based on optimization method and the results have been tabulated in Table 1 and 2 for b=1.0, 1.5, 2.0 and 2.5. In most activation energy equations, the coefficients $C_{\alpha x}$ and $D_{\alpha x}$ are considered to be independent of a. Obviously both coefficients are dependent on a, but the dependence of $C_{\alpha x}$ is very weak with compared to $D_{\alpha x}$ dependence on a.

(a)

(b)

(c)
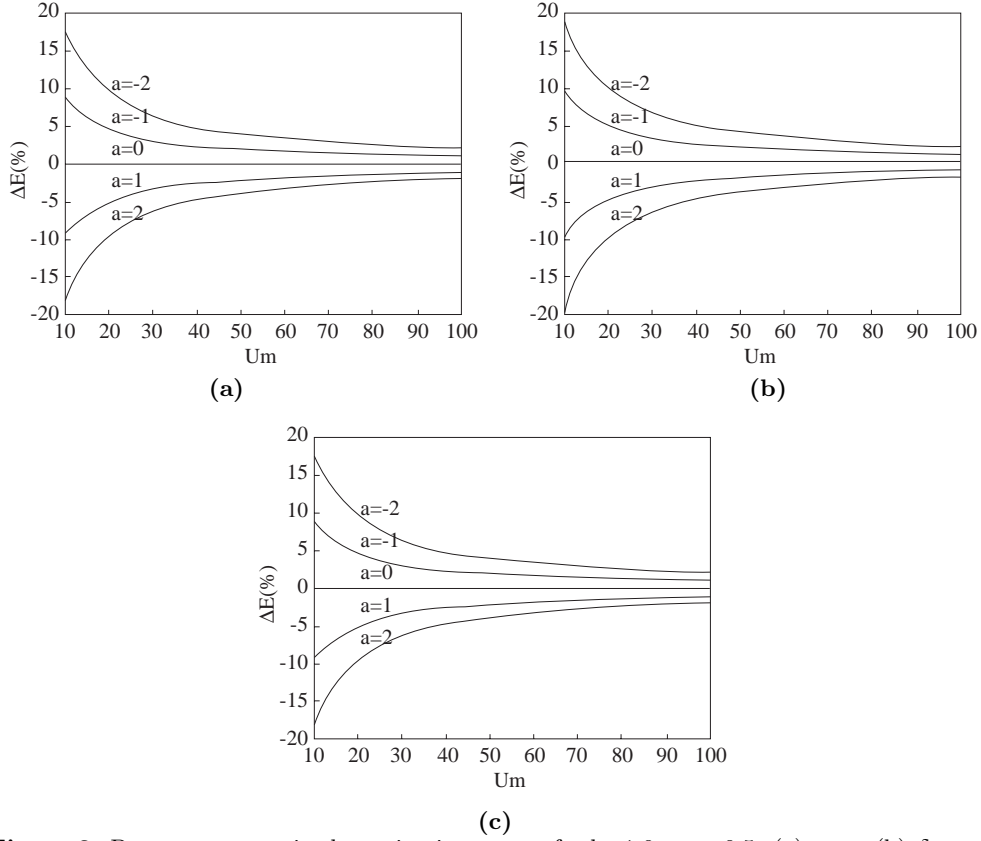
Figure 3. Percentage error in the activation energy for b=1.0 at x=0.5. (a) $\tau_{1/2}$, (b) $\delta_{1/2}$ and (c) $\omega_{1/2}$

4. Conclusion

In conclusion, it should be emphasized here that any error in the evaluation of E introduces a much higher error in the determination of S_0. Therefore, the temperature dependency of the frequency factor should be considered in the analysis of the thermoluminescence glow peaks, otherwise significant errors may occur in the calculation of trapping parameters.

Table 1. The values of coefficients $C_{\alpha x}$ and $D_{\alpha x}$ in the peak shape formula for different order kinetics at x=0.50

	b	$\tau_{1/2}$	$\delta_{1/2}$	$\omega_{1/2}$
$C_{\alpha x}$	1.0	1.46013-0.00122a	0.98519-0.00009a	2.44342-0.00091a
	1.5	1.62676-0.00150a	1.38613-0.00028a	3.01006-0.00130a
	2.0	1.75930-0.00170a	1.76218-0.00060a	3.51802-0.00179a
	2.5	1.87026-0.00188a	2.12396-0.00101a	3.99047/0.00240a
$D_{\alpha x}$	1.0	-1.08475-0.46690a	-0.08773-0.49681a	-0.65339-0.48311a
	1.5	-1.31820-0.46171a	-0.22064-0.49249a	-0.77690-0.48008a
	2.0	-1.52325-0.45788a	-0.38681-0.48708a	-0.91611-0.47637a
	2.5	-1.70818-0.45437a	-0.57738-0.48125a	-0.06966-0.47204a

Table 2. The values of coefficients $C_{\alpha x}$ and $D_{\alpha x}$ in the peak shape formula for different order kinetics at x=0.75

	b	$\tau_{1/2}$	$\delta_{1/2}$	$\omega_{1/2}$
$C_{\alpha x}$	1.0	0.86727-0.00056a	0.67349-0.00012a	1.54030-0.00056a
	1.5	0.99419-0.00074a	0.89707-0.00027a	1.89056-0.00086a
	2.0	1.09655-0.00089a	1.09765-0.00046a	2.19339-0.00123a
	2.5	1.18328-0.00105a	1.28379-0.00067a	2.46622-0.00162a
$D_{\alpha x}$	1.0	-0.83819-0.47448a	-0.21305-0.49318a	-0.5505-0.48461a
	1.5	-1.07859-0.46890a	-0.39558-0.48793a	-0.74043-0.47998a
	2.0	-1.29526-0.46441a	-0.59693-0.48248a	-0.93142-0.47493a
	2.5	-1.49464-0.45988a	-0.81108-0.47710a	-1.12528-0.46996a

Acknowledgment

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