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Reliability Criteria for Testing the Goodness of the Activation Energy Values Obtained by the Peak Shape Methods in Thermoluminescence Experiments

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Abstract: The aim of this study is to give some expressions able to give a criteria of acceptance for the activation energy values determined through the so called peak shape methods. The expressions are derived for both first and second order kinetics. Furthermore, using approximations concerning the peak temperature parameters, the reliability expressions are simplified for getting a more quickly criteria of acceptance. A table lists several data, from literature, concerning the activation energy determined for various Thermoluminescence materials; the experimental values are then tested using the criteria of acceptance showing the goodness of the method here presented in this research.

Key words: Thermoluminescence, peak shape methods, activation energy, acceptance criteria, first and second order kinetics

INTRODUCTION

An important and widely used method for investigating the trapping levels in crystals is based on the Thermoluminescence (TL) technique. One of the most convenient way, among the various TL methods introduced during the years, is based on the geometrical characterization of a TL glow peak, i.e. the very well known Peak Shape (PS) methods. In fact, for calculating the activation energy of the trapping level corresponding to a peak in the glow curve, one needs to measure three temperature values on the peak itself: the temperature at the maximum, T_M and the first and second half temperatures, T_1 and T_2, respectively on the ascending and descending parts of the peak.

The formulas proposed for finding the activation energy usually include the following factors:

$\tau = T_M - T_1$ the half width at the low temperature side of the peak,

$\delta = T_2 - T_M$ the halfwidth towards the falloff of the peak,

$\omega = T_2 - T_1$ the total halfwidth (FWHM).

In the following is given a list of the various expressions, for both first and second order of kinetics, allowing for the activation energy determination. All the expressions have been modified by Chen[1] for getting a better accuracy in the E values.

Grosswiener[2]:

$$\text{1st} \quad \text{Order} \quad (E_G)_\tau = 1.41k\frac{T_1 T_M}{\tau} \qquad (1)$$

$$\text{2nd} \quad \text{Order} \quad (E_G)_\tau = 1.68k\frac{T_1 T_M}{\tau} \qquad (2)$$

The coefficient 1.41 in Eq.1 was computed by Dussel and Bube[3].

Lushchik[4]:

$$\text{1st} \quad \text{Order} \quad (E_L)_\delta = 0.976\frac{kT_M^2}{\delta} \qquad (3)$$

$$\text{2nd} \quad \text{Order} \quad (E_L)_\delta = 1.706\frac{kT_M^2}{\delta} \qquad (4)$$

Halperin and Braner[5]:

$$\text{1st} \quad \text{Order} \quad (E_{HB})_\tau = 1.72\frac{kT_M^2}{\tau}(1-1.58\Delta_M) \qquad (5)$$

$$\text{2nd} \quad \text{Order} \quad (E_{HB})_\tau = \frac{2kT_M^2}{\tau}(1-3\Delta_M) \qquad (6)$$

Where, $\Delta_M = 2kT_M/E$.

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Both Eq. 5 and 6 require an iterative process owing the presence of the quantity Δ_M. To avoid this difficulty, Chen modified them as following:

$$1st \quad Order \qquad (E_{HB})_\tau = 1.52\frac{kT_M^2}{\tau} - 3.16kT_M \quad (7)$$

$$2nd \quad Order \qquad (E_{HB})_\tau = 1.813\frac{kT_M^2}{\tau} - 4kT_M \quad (8)$$

Chen also gave two more expressions based on the ω factor:

Chen's additional expressions:

$$1st \quad Order \quad \left(E_{C_{aux}}\right)_\omega = 2.29 \cdot \frac{T_M^2}{\omega} \qquad (9)$$

$$2nd \quad Order \quad \left(E_{C_{aux}}\right)_\omega = 2kT_M\left(1.756\frac{T_M}{\omega} - 1\right) \qquad (10)$$

Balarin: Balarin[6] gave expressions based on the three temperatures T_1, T_2 and T_M:

$$1st \quad Order \qquad (E_B)_\omega = \frac{T_M^2}{4998 \cdot \omega} \qquad (11)$$

$$2nd \quad Order \qquad (E_B)_\omega = \frac{T_M^2}{3542 \cdot \omega} \qquad (12)$$

Chen's expressions (general): The previous methods were summed up by Chen[7], who considered a general order kinetics, l, ranging from 1 to 2, then giving the possibility of non-integer values for the kinetics order. The general expression is

$$E_\alpha = c_\alpha\left(\frac{kT_M^2}{\alpha}\right) - b_\alpha(2kT_M) \qquad (13)$$

Where, α is τ, δ or ω. The values of c_α and b_α are summarized as:

$$c_\tau = 1.51 + 3.0(\mu - 0.42) \quad b_\tau = 1.58 + 0.42(\mu - 0.42)$$

$$c_\delta = 0.976 + 7.3(\mu - 0.42) \qquad b_\delta = 0$$

$$c_\omega = 2.52 + 10.2(\mu - 0.42) \qquad b_\omega = 1$$

with

$$\mu = \frac{\delta}{\omega} = \frac{T_2 - T_M}{T_2 - T_1}$$

being $\mu = 0.42$ for a first order kinetics and $\mu = 0.52$ for a second order.

The previous general expression, developed just for the 1st and the 2nd orders, gives:

1st Order

$$(E_C)_\tau = 1.51\frac{kT_M^2}{\tau} - 3.04kT_M \qquad (14)$$

$$(E_C)_\delta = 0.976\frac{kT_M^2}{\delta} \qquad (15)$$

$$(E_C)_\omega = 2.52\frac{kT_M^2}{\omega} - 2kT_M \qquad (16)$$

2nd Order

$$(E_C)_\tau = 1.81\frac{kT_M^2}{\tau} - 4kT_M \qquad (17)$$

$$(E_C)_\delta = 1.706\frac{kT_M^2}{\delta} \qquad (18)$$

$$(E_C)_\omega = 3.54\frac{kT_M^2}{\omega} - 2kT_M \qquad (19)$$

Comparison among the peak shape expressions: The variability of the E values determined using the various peak shape expressions was checked at first.

Synthetic glow curves following a first or a second order kinetics were generated for various values of E, keeping s constant and then for various values of s, keeping then E constant. After that, to the so generated glow curves the various peak shape methods have been applied.

It was observed that the E values calculated by the H-B expressions are always bigger than the other values. Furthermore, values more closed to the assigned E are obtained by the G, L and C_δ expressions.

Reliability expressions: From a theoretical point of view the various PS method do not give the same values for E because, mainly, the expressions were obtained according to different theoretical procedures as well as different approximations; furthermore, they are based on specific characteristics of the glow peak. Therefore, it seems to be correct to compare the E values obtained from expressions based on the same peak parameters, so that the relations obtained in this way could act as a test of acceptance for the E values.

The expressions so far given have been handled for getting a criteria of reliability of the E values obtained using the PS methods. In most of the cases the Chen's expressions have been used as reference because they have a more general meaning respect to the others and also give more accurate values of E.

1st Order

$$\left(\frac{E_L}{E_C}\right)_\delta = \frac{0.978K\dfrac{T_M^2}{\delta}}{0.976K\dfrac{T_M^2}{\delta}} = 1.002 \qquad (20)$$

$$\left(\frac{E_G}{E_C}\right)_\tau = \frac{1.41K\dfrac{T_M T_1}{\tau}}{1.51K\dfrac{T_M^2}{\tau} - 3.16KT_M}$$
$$= \frac{T_1}{1.07\left(2.09T_1 - 1.09T_M\right)} \qquad (21)$$

$$\left(\frac{E_{HB}}{E_C}\right)_\tau = \frac{\dfrac{1.72kT_M^2}{\tau}(1-1.58\Delta_M)}{\dfrac{1.51kT_M^2}{\tau} - 3.16kT_M} = 1.139\frac{1-1.58\Delta_M}{1-2.093\dfrac{T_M - T_1}{T_M}}$$

Because the presence of the term Δ_M in the last expression, we need to calculate its limits of validity:

$$\Delta_M = 0 \rightarrow \frac{1.139}{1 - 2.039\dfrac{T_M - T_1}{T_M}} = \frac{1.042}{1.915\dfrac{T_1}{T_M} - 1}$$

$$\Delta_M = 0.1 \rightarrow \frac{0.959}{1 - 2.093\dfrac{T_M - T_1}{T_M}} = \frac{0.877}{1.915\dfrac{T_1}{T_M} - 1}$$

and then

$$\left(\frac{0.877}{1.915\dfrac{T_1}{T_M} - 1}\right)_{\Delta_M = 0.1} \leq \left(\frac{E_{HB}}{E_C}\right)_\tau \leq \left(\frac{1.042}{1.915\dfrac{T_1}{T_M} - 1}\right)_{\Delta_M = 0} \qquad (22)$$

$$\left(\frac{E_G}{E_{HB}}\right)_\tau = \frac{1.41k\dfrac{T_1 T_M}{\tau}}{1.72\dfrac{kT_M^2}{\tau}\left(1 - 1.58\Delta_M\right)} = \frac{0.8198 \cdot T_1}{T_M\left(1 - 1.58\Delta_M\right)}$$

In this case also it is necessary to calculate the limits of validity of the expression. Then, we obtain:

$$\Delta_M = 0 \rightarrow 0.8198\frac{T_1}{T_M}$$

$$\Delta_M = 0.1 \rightarrow 0.9736\frac{T_1}{T_M}$$

and then

$$\left(0.8198\frac{T_1}{T_M}\right)_{\Delta_M = 0} \leq \left(\frac{E_G}{E_{HB}}\right)_\tau \leq \left(0.9736\frac{T_1}{T_M}\right)_{\Delta_M = 0.1} \qquad (23)$$

2nd Order

$$\left(\frac{E_L}{E_C}\right)_\delta = \frac{1.706 \cdot \dfrac{kT_M^2}{\delta}}{1.71 \cdot \dfrac{kT_M^2}{\delta}} = 0.998 \qquad (24)$$

$$\left(\frac{E_G}{E_C}\right)_\tau = \frac{1.68k \cdot \dfrac{T_M \cdot T_1}{\tau}}{1.81k \cdot \dfrac{T_M^2}{\tau} - 4kT_M} = \frac{0.7671 \cdot T_1}{1.8265 \cdot T_1 - T_M} \qquad (25)$$

$$\left(\frac{E_{HB}}{E_C}\right)_\tau = \frac{\dfrac{2kT_M^2}{\tau}\left(1 - 3\Delta_M\right)}{1.81\dfrac{kT_M^2}{\tau} - 4kT_M} = 0.917 \cdot \frac{1 - 3\Delta_M}{1.83 \cdot \dfrac{T_1}{T_M} - 1}$$

Limits:

$$\Delta_M = 0 \rightarrow \frac{0.917 \cdot T_M}{1.83 \cdot T_1 - T_M}$$

$$\Delta_M = 0.1 \rightarrow \frac{0.7 \cdot T_M}{1.83 \cdot T_1 - T_M}$$

so that

$$\left(\frac{0.7 \cdot T_M}{1.83 \cdot T_1 - T_M}\right)_{\Delta_M = 0.1} \leq \left(\frac{E_{HB}}{E_C}\right)_\tau \leq \left(\frac{0.917 \cdot T_M}{1.83 \cdot T_1 - T_M}\right)_{\Delta_M = 0} \qquad (26)$$

$$\left(\frac{E_G}{E_{HB}}\right)_\tau = \frac{1.68k \cdot \dfrac{T_M \cdot T_1}{\tau}}{\dfrac{2kT_M^2}{\tau}\left(1 - 3\Delta_M\right)} = \frac{0.84 \cdot T_1}{T_M\left(1 - 3\Delta_M\right)}$$

limits:

$$\Delta_M = 0 \rightarrow 0.84 \cdot \frac{T_1}{T_M} \quad \Delta_M = 0.1 \rightarrow 1.2 \cdot \frac{T_1}{T_M}$$

so that

$$\left(0.84 \cdot \frac{T_1}{T_M} \right)_{\Delta_M=0} \leq \left(\frac{E_G}{E_{HB}} \right)_\tau \leq \left(1.2 \cdot \frac{T_1}{T_M} \right)_{\Delta_M=0.1} \quad (27)$$

The expressions containing the parameter ω are based on the three temperature values T_1, T_2 and T_M. For getting the reliability expressions in this case, it is better to have only two temperature values, as in the previous expressions. For this purpose, one can consider the asymmetrical and symmetrical properties of a glow peak following a first or a second order kinetics respectively. Then, using the synthetic glow-peaks previously generated, some relations among the three temperatures T_1, T_2 and T_M can be obtained. As a convenient first approximation, one may take $0.95\ T_M$ for T_1 in both first and second order peaks, $T_2 = 1.036\ T_M$ and $T_2 = 1.054\ T_M$, respectively for first and a second order peaks.

The following expressions can be then obtained:

1st order

$$\left(\frac{E_B}{E_C} \right)_\omega = \frac{\dfrac{T_M^2}{4998(T_2 - T_1)}}{2.52 \dfrac{kT_M^2}{T_2 - T_1} - 2kT_M}$$

from which, using the approximation $T_1 = 0.95\ T_M$, the following expression, as a function of T_M and T_2, is obtained:

$$\left(\frac{E_B}{E_C} \right)_\omega = \frac{1.16 \cdot T_M}{2.21 \cdot T_M - T_2} \quad (28)$$

Using the approximation $T_2 = 1.036\ T_M$, the following expression is also obtained:

$$\left(\frac{E_B}{E_C} \right)_\omega = \frac{1.16 \cdot T_M}{0.224 \cdot T_M + T_1} \quad (29)$$

2nd order

$$\left(\frac{E_B}{E_C} \right)_\omega = \frac{\dfrac{T_M^2}{3542 \cdot (T_2 - T_1)}}{\left(\dfrac{3.54 \cdot T_M^2}{(T_2 - T_1)} - 2T_M \right) \cdot k}$$

from which, using the approximation $T_1 = 0.95\ T_M$, we get

$$\left(\frac{E_B}{E_C} \right)_\omega = \frac{1.64 \cdot T_M}{2.72 \cdot T_M - T_2} \quad (30)$$

As before, using now the approximation $T_2 = 1.054\ T_M$, the expression as a function of T_M and T_1 is obtained:

$$\left[\left(\frac{E_B}{E_C} \right)_\omega = \frac{1.64 \cdot T_M}{0.716 \cdot T_M + T_1} \right] \quad (31)$$

Approximated expressions: Using the approximations of T_1 and T_2 as a function of T_M, the previous expressions of reliability can be furthermore simplified.

1st order

$$\left(\frac{E_G}{E_C} \right)_\tau = 0.992 \quad (32)$$

$$1.071 \leq \left(\frac{E_{HB}}{E_C} \right)_\tau \leq 1.272 \quad (33)$$

$$0.779 \leq \left(\frac{E_G}{E_{HB}} \right)_\tau \leq 0.928 \quad (34)$$

$$\left(\frac{E_B}{E_C} \right)_\omega = 1.014 \quad (35)$$

2nd order

$$\left(\frac{E_G}{E_C} \right)_\tau = 0.991 \quad (36)$$

$$0.948 \leq \left(\frac{E_{HB}}{E_C} \right)_\tau \leq 1.242 \quad (37)$$

$$0.798 \leq \left(\frac{E_G}{E_{HB}} \right)_\tau \leq 1.140 \quad (38)$$

$$\left(\frac{E_B}{E_C} \right)_\omega = 0.991 \quad (39)$$

Table 1: The goodness of the experimental values of E, determined using the peak shape methods, is tested according the reliability expressions given in the text. The columns calculated limits and approximated limits give the range of acceptance for the expected values of the activation energy. The column experimental ratios lists the ratios calculated using the experimental values of E

Materials	Peak No.	Kinetics order, b	T_1 (K)	T_M (K)	T_2 (K)	E (eV)	Ref.	Reliability expression	Calculated limits	Approximated limits	Experimental ratios
CaF$_2$: Tm	3	1st	418.4	437.8	408.5	$(E_L)_\delta = 1.20$	[8]	(20)	1.002		1.000
						$(E_{HB})_\tau = 1.18$		(22)	1.056-1.255	1.071-1.272	1.073
						$(Ec)_\tau = 1.20$					
						$(Ec)_\tau = 1.10$					
						$(Ec)_\omega = 1.10$					
	5	2nd	501.7	523.0	547.7	$(E_L)_\delta = 1.62$		(24)	0.998		0.853
						$(E_{HB})_\tau = 1.82$		(26)	0.927-1.214	0.948-1.242	1.071
						$(Ec)_\delta = 1.90$					
						$(Ec)_\tau = 1.70$					
						$(Ec)_\omega = 1.80$					
KMgF$_3$: La	1	2nd	409.8	434.5	461	$(E_G)_\tau = 1.04$	[9]	(25)	1.001	0.991	1.000
						$(E_L)_\delta = 1.03$		(24)	0.998		1.000
						$(E_{HB})_\tau = 1.04$		(26)	0.964-1.263	0.948-1.242	1.000
						$(E_B)_\omega = 1.03$		(30)	0.989	0.991	0.990
								(31)	0.988	0.991	
						$(E_c)_\delta = 1.03$					
						$(E_C)_\tau = 1.04$					
						$(E_C)_\omega = 1.04$					
KMgF$_3$: Ce (1.0 M%)	Dos Peak	$\cong$2nd	469	500	534	$(E_G)_\tau = 1.10$	[10]	(25)	1.009	0.991	1.019
						$(E_L)_\delta = 1.08$		(24)	0.998		1.000
						$(E_{HB})_\tau = 1.09$		(26)	0.977-1.280	0.948-1.242	1.000
						$(E_B)_\omega = 1.09$		(30)	0.993	0.991	1.005
								(31)	0.992	0.991	
						$(E_C)_\delta = 1.08$					
						$(E_C)_\tau = 1.08$					
						$(E_C)_\omega = 1.08$					

Reliability of the method and conclusions: Table 1 lists some activation energy values from literature as well as the results obtained using the present method. The tenth column lists the limits of reliability as obtained inserting the glow peak temperatures in the various expressions. The experimental ratios are obtained as the ratios of the calculated E values. For instance, it can be observed that the $(E_L)\delta$ value, calculated for the 5th peak in CaF$_2$: Tm, is much lower compared to the other E values for the same peak. The experimental ratio $(E_L/E_C)\delta$ is very low, about 15% less than the calculated limit using the peak temperatures data. In this case, it seems to be correct to reject the activation energy data obtained using the Lushchik expression. In general, the E values calculated for the different materials listed in Table 1 are in good agreement among them, according to both calculated limits and experimental ratios.

The column of approximated limits shows the limits obtained using the values of T_1 and T_2 as function of T_M. Also in this case it can be observed a quite good agreement between the experimental ratios and the approximated limits.

The method here presented gives a good way for testing the reliability of the experimental activation energy findings.

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