JOURNAL OF MECHANICS OF CONTINUA AND MATHEMATICAL SCIENCES
www.journalimcms.org

ISSN (Online) : 2454 -7190 Vol.-16, No.-7, July (2021) pp 1-8 ISSN (Print) 0973-8975

ANALYSIS OF THERMOLUMINESCENCE GLOW CURVES RECORDED UNDER THE HYPERBOLIC HEATING SCHEME BY USING AN ALTERNATIVE CONCEPT OF SYMMETRY

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https://doi.org/10.26782/jmcms.2021.07.00001

(Received: May 14, 2021; Accepted: June 30, 2021)

Abstract

Usually, the order of kinetics of thermoluminescence (TL) glow curve is evaluated by using the concept of traditional symmetry factor (μ_g) in which only three points of a glow curve are used. From the statistical point of view of the reliability of any method of analysis of the glow, curve improves if instead of a few points the method can use a larger portion of the glow curve. In the present work, a technique is proposed to determine the order of kinetics associated with a TL peak by using the concept of skewness. The method is applied to experimental thermoluminescence (TL) curves recorded in a hyperbolic heating scheme.

Keywords: Thermoluminescence, hyperbolic heating scheme, skewness, order of kinetics

I. Introduction

Thermoluminescence (TL) is exhibited by semiconducting materials and insulators on controlled heating after irradiation by some kind of ionizing radiation such as γ-rays, β-rays, x-rays, etc. The technique of TL has been extensively applied to the fields of Dating and Dosimetry [III, IX]. The simplest model of analysis of TL is the kinetic order model (KOM) [III, IX]. KOM incorporates the first-order kinetics model (FOKM) of Randal and Wilkins [V], the second-order kinetics model (SOKM) of Garlick and Gibson [IV] and the general order kinetics model (GOKM) of Chen [X]. In KOM, TL has been explained by three trapping parameters namely activation energy (E), order of kinetics (b) and frequency factor (s) [III, IX, X]. There exists a number of methods [IX, X, XIII] of analysis of TL phenomenon namely initial rise, various heating rates peak shape, isothermal decay and curve-fitting, etc. Unfortunately, except for isothermal decay [XI] and curve-fitting [IX, XI], there is no rigorous method of determination of the order of kinetics associated with a TL peak. Normally a preliminary estimation of the order of kinetics is carried out by using the concept of symmetry factor [XI] which uses only three points of a TL peak. For this purpose, skewness is a suitable parameter because it uses a larger portion of a TL glow curve to indicate its symmetry. In the present paper, we apply the concept of skewness to evaluate the order of kinetics of a TL glow curve recorded in a hyperbolic heating scheme (HHS) [XIV, XV]. TL using HHS has been analyzed by Azharuddin et al.[XV]. Finally, we have analyzed the applicability of our findings by considering experimental TL peaks recorded under HHS [XV] represented by

$$\frac{1}{T} = \frac{1}{T_0} - \beta' t \tag{1}$$

Where T is the temperature at t, T_0 is the initial temperature, β' is the heating constant bearing unit $K^{-1}s^{-1}$.

II.i. Theoretical analysis of TL recorded in the hyperbolic heating scheme (HHS)

According to Azharuddin et al [XV] for a TL peak recorded under HHS, the fractional intensity can be written as (for first-order kinetics i.e. $b = 1$)

$$\frac{I}{I_m} = \exp\,[u_m - u + F(u, u_m)] \tag{2}$$

For non-first order kinetics, it is possible to write [XV]

$$\frac{I}{I_m} = \exp(u_m - u)\left[1 - \frac{b-1}{b}\,F(u, u_m)\right]^{\frac{-b}{b-1}} \tag{3}$$

With $u = \frac{E}{kT}$ and $u_m = \frac{E}{kT_m}$

I is the TL intensity at temperature T and I_m is the peak intensity at a temperature T_m, $x = \frac{I}{I_m}$ is the fractional intensity, E is the activation energy and k is the Boltzmann constant.

$$F(u, u_m) = 1 - \exp\,(u_m - u) \tag{4}$$

Using equations (1) and (2) it is possible to evaluate temperatures T_x^- and T_x^+ corresponding to the fractional intensity $x = \frac{I}{I_m}$ in the rising and falling sides of a TL peak by an iterative method. [XII, XV].

$$T = T_x^- \quad \text{for} \quad T_x^- < T_m \tag{5}$$

$$T = T_x^+ \quad \text{for} \quad T_x^+ > T_m \tag{6}$$

$$T_x^{\pm} = \frac{E}{kb_x^{\pm}} \tag{7}$$

II.ii. Concept of skewness:

Skewness [VII, VIII] is the degree of asymmetry of any distribution. If the frequency curve of distribution has a larger tail to the right of the minimum than to the left of the distribution it is said to be skewed to the right or have positive skewness. If the reverse happens it is said to be skewed to the left or negatively skewed. Asymmetric distribution has zero skewness. The r[th] moment about an arbitrary origin is defined as [VII, VIII]

$$m_r = \frac{1}{N}\sum_{i=1}^{N}(x_i - \bar{x})^r \tag{8}$$

The odd number central moments are positive for positively skewed distribution, zero for symmetric distributions and negative for negatively skewed distribution. Skewness is defined as [VII, VIII]

$$s_k = \frac{m_3}{\Delta^3} \tag{9}$$

Where m_3 is the third order moment about the mean given by [VII, VIII]

$$m_3 = \frac{1}{N}\sum_{i=1}^{N}(x_i - \bar{x})^3 \tag{10}$$

Where $\bar{x}$ is the mean. N is the number of data points and Δ is the standard deviation.

II.iii. Calculation of skewness of TL curve recorded under HHS:

In the TL curve, we consider the intensity (I) and temperature (T) curves so that the independent variable is T and the dependent variable is I. From equation (9) the skewness $s_k(x)$ corresponding to the fractional intensity $x = \frac{I}{I_m}$ is given by

$$s_k(x) = \frac{c}{d} \tag{11}$$

Where

$$c = \sum_{i=1}^{N}\frac{(T_x^{\pm} - \bar{T})^3}{N} \tag{12}$$

And

$$d = \left[\sum_{i=1}^{N}\frac{(T_x^{\pm} - \bar{T})}{N}\right]^{\frac{3}{2}} \tag{13}$$

$\bar{T}$ is the average of all the temperatures considered. For a particular value of the order of kinetics (b) one can calculate T_x^- and T_x^+ for arbitrary values of x by using equations (2-7). For example, to calculate $s_k(x)$ for $x = 0.5$ and any particular value of b one has to calculate the temperatures

$T_{0.50}^-, T_{0.55}^-$

$T_{0.60}^-, T_{0.65}^-, T_{0.70}^-, T_{0.75}^-, T_{0.80}^-, T_{0.85}^-, T_{0.90}^-, T_{0.95}^-,$

$T_{0.95}^+, T_{0.90}^+, T_{0.85}^+, T_{0.80}^+, T_{0.75}^+, T_{0.70}^+, T_{0.65}^+, T_{0.60}^+, T_{0.55}^+, T_{0.50}^+$, where superscripts $(\mp)$ correspond to rising and falling tides of the TL peak respectively. In this way, it is possible to calculate $s_k(x)$ for other values of x, namely $x = 0.6667$ and $x = 0.8$ for an arbitrary value of b.

III. Results and Discussion:

It is found that for a particular value of x, $s_k(x)$depends on both $b$and the quantity $u_m = \frac{E}{kT_m}$. But the dependence of $s_k(x)$ on b is stronger than that on u_m. For 1≤ $b \leq 2$and $10 \leq u_m \leq 100$, $s_k(x)$ has been calculated for x= 0.5, 0.6667 and 0.8. For $b = 1$, $s_k(0.5)$ varies from -0.058 and -0.141 as $u_m$changes from 10 to 100 for $b = 2$, $s_k(0.5)$ changes from 0.075 to 0.009 for $10 \leq u_m \leq 100$. The values of $s_k(0.5)$ for different values of u_m and for $b = 1, 1.5$ and 2 are presented in Table 1. As $s_k(x)$ depends both on the order of kinetics b and $u_m = \frac{E}{kT_m}$ so for a particular value of x and b we have calculated the average value of $s_k(x)$ for a particular value of b within the range $10 \leq u_m \leq 100$, which is given by

$$\bar{s_k}(x) = \frac{1}{90}\int_{10}^{100} s_k\,(x)du_m \tag{14}$$

To increase the accuracy of the evaluation of the integral in equation (14) the range of integration (10, 100) is divided into a number of sub-ranges namely (10, 20), (20, 30), (30, 40), (40, 50), (50, 60), (60, 70), (70, 80), (80, 90) and (90, 100). The integral over each sub-range has been carried out by using 16-point Gauss-Legendre quadrature [XVI]. In Table 2, we have depicted the values of $\bar{s_k}(0.5)$ with an order of kinetics (b) for 1≤ $b \leq 2$. It is evident from Table 2 that $\bar{s_k}(0.5)$ changes sign around $b = 1.7$ to 1.8 as b increases from 1 to 2 so as b changes from 1 to 2, TL curve changes from asymmetric to symmetric type. So it is evident that skewness is both a quantitative and qualitative indicator of the symmetry of a TL curve we also depict the variation of $\bar{s_k}(0.6667)$and $\bar{s_k}(0.8)$ with an order of kinetics b in Table 2. Like $\bar{s_k}(0.5)$, the signs of $\bar{s_k}(0.6667)$and $\bar{s_k}(0.8)$ change from negative to positive as b changes from 1 to 2. We have calculated the values of $\bar{s_k}(0.6667)$ and $\bar{s_k}(0.8)$ because the upper portion of a TL curve is less affected by satellite peaks.

Finally by using the statistical technique of least square quadratic fitting [VII] $\bar{s_k}(0.5)$, $\bar{s_k}(0.6667)$and $\bar{s_k}(0.8)$ have been as a quadratic function of b given by

$$\bar{s_k}(0.5) = -0.3758 + 0.3081b - 0.0475b^2 \tag{15}$$

$$\bar{s_k}(0.6667) = -0.2457 + 0.2043b - 0.0329b^2 \tag{16}$$

$$\bar{s_k}(0.8) = -0.1033 + 0.0866b - 0.0143b^2 \tag{17}$$

Order of kinetics b of a TL peak can be evaluated by using equations (15)-(17)

IV. Determination of the order of kinetics (b) of some experimental TL peaks recorded under the hyperbolic heating scheme by using the concept of skewness

We consider two TL peaks recorded under HHS by Ziriker et al [XVI]. The peaks are (i) 444.8K TL peak of X-irradiated Al_2O_3 and (ii) 375.5K TL peak of spicer I sample of MgO irradiated by X-rays. The heating content for the hyperbolic profile is $\beta' = 1.3 \times 10^{-6} K^{-1} s^{-1}$. In table 3, the values of $s_k(0.5)$, $s_k(0.6667)$ and $s_k(0.8)$

for 444.7K TL peak of X-irradiated Al_2O_3 are presented. The values of the order of kinetics obtained using equations (15)-(17) are also shown in table 3. The closeness of the values of the order of kinetics from $s_k(0.5)$, $s_k(0.6667)$ and $s_k(0.8)$ indicates their internal consistency. The average value of the order of kinetics as calculated by different s_k values is 1.85 ± 0.03. This is in fair agreement with the reported value $b = 2.0$ [XVI].

Finally, we consider the 375.5K TL peak of spicer-I [XVI] variety of MgO irradiated by X-rays and recorded under the hyperbolic heating scheme with heating constant $\beta' = 1.3 \times 10^{-6} K^{-1} s^{-1}$. The values of $s_k(0.5)$, $s_k(0.6667)$ and $s_k(0.8)$ and associated values of b are presented in table 3. In this case also the average value of the order of kinetics as calculated from different s_k values are 1.07 ± 0.02. Here also we obtain a reasonably fair agreement between the calculated and reported value of b namely $b = 1.0$ [XVI].

V. Conclusion:

In the present paper, the skewness of TL peaks recorded under hyperbolic heating profile has been studied. In statistics, skewness is an indicator of the symmetry of a curve. If a curve is skewed to the right skewness is positive and if it is skewed to the left skewness is negative. This is manifested by the fact that the skewness of the first-order TL peak is negative and as the order of kinetics increases from 1 to 2, skewness gradually becomes positive. Apart from the order of kinetics skewness is weakly dependent on $u_m = \frac{E}{kT_m}$. So skewness can indicate the order of kinetics of a TL peak but because of the weak dependence of skewness on u_m error creeps in the determination of b. This is evident from our values of b for experimental TL peaks (Table 3). Skewness is a more reliable indicator of the order of kinetics compared with the conventional symmetry factor [XI] which uses only three points of a glow curve. From a statistical point of view, skewness is a more reliable indicator of the symmetry of a glow curve because the evaluation of skewness requires a larger portion of the TL glow curve. Since a TL peak is usually accompanied by satellite for evaluation of skewness one should use the upper portion of the TL curve which is relatively less affected by satellite peaks. Because of this apart from $s_k(0.5)$, $s_k(0.6667)$ and $s_k(0.8)$ have been calculated.

The agreement of the values of the order of kinetics b calculated by using $s_k(0.5)$, $s_k(0.6667)$ and $s_k(0.8)$ for experimental TL peaks indicate the consistency of the value of b obtained by using skewness. Skewness is also a qualitative indicator of the symmetry of the glow curve because it changes signs around $b \approx 1.7$ to 1.8. So skewness of a TL peak can be used to determine the order of kinetics.

Table 1: $s_k(0.5)$ vs u_m corresponding to hyperbolic heating scheme for b = 1, 1.5 and 2

u_m	$b = 1.0$	$b = 1.5$	$b = 2.0$
10	-0.0577	0.0547	0.1453
15	-0.0878	0.0153	0.0953
20	-0.1032	-0.0042	0.0711
25	-0.1125	-0.0160	0.0567
30	-0.1187	-0.0238	0.0472
35	-0.1232	-0.0294	0.0404
40	-0.1266	-0.0336	0.0354
45	-0.1292	-0.0369	0.0314
50	-0.1313	-0.0395	0.0283
55	-0.1331	-0.0417	0.0257
60	-0.1345	-0.0435	0.0236
65	-0.1357	-0.0450	0.0218
70	-0.1368	-0.0463	0.0202
75	-0.1377	-0.0474	0.0188
80	-0.1385	-0.0484	0.0177
85	-0.1392	-0.0493	0.0166
90	-0.1398	-0.0501	0.0157
95	-0.1404	-0.0507	0.0148
100	-0.1409	-0.0514	0.0141

Table 2: $\overline{s_k}(0.5)$, $\overline{s_k}(0.6667)$and $\overline{s_k}(0.8)$ as a function of the order of kinetics b for the hyperbolic heating scheme.

b	$\bar{s_k}(0.5)$	$\bar{s_k}(0.6667)$	$\bar{s_k}(0.8)$
1	-0.1161	-0.0705	-0.0314
1.1	-0.0941	-0.0606	-0.0253
1.2	-0.0737	-0.0475	-0.0198
1.3	-0.0548	-0.0353	-0.0147
1.4	-0.0372	-0.0240	-0.0100
1.5	-0.0206	-0.0135	-0.0057
1.6	-0.0048	-0.0035	-0.0016
1.7	0.0101	0.0059	0.0023
1.8	0.0244	0.0149	0.0060
1.9	0.0381	0.0235	0.0095
2.0	0.0512	0.0316	0.0129

Table 3. Skewness and order of kinetics of some experimental TL peaks were recorded with the hyperbolic heating scheme.

Specification of the peak	Reported kinetic parameters of the peak [XVI]			$s_k(x)$			b calculated from skewness			Mean b
	E (eV)	s sec^{-1}	b	$s_k(0.5)$	$s_k(0.6667)$	$s_k(0.8)$	Using $s_k(0.5)$	Using $s_k(0.6667)$	Using $s_k(0.8)$	
444.7K TL peak of X-irradiated Al_2O_3	1.30	10^{13}	2.0	0.0417	0.0258	0.0105	1.93	1.91	1.93	1.92 ±0.01
375.5K TL peak of spicer-I variety of MgO irradiated with X-rays	0.97	10^{12}	1.0	-0.1205	-0.0325	-0.0778	1.01	1.00	1.01	1.01 ±0.01

Conflicts of Interest:

The authors declare that they have no conflicts of interest to report regarding the present study.

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