EVALUATING TRAP PARAMETERS OF THERMOLUMINESCENCE GLOW-CURVES CONSIDERING TEMPERATURE DEPENDENT FREQUENCY FACTOR

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Abstract
First and general order thermoluminescence glow curves were simulated in a MATLAB environment. The simulated curves considered the case when the pre-exponential or frequency factor is temperature dependent for kinetic orders ranging from 1.0 to 2.0. For each order the temperature dependent index was varied from -1 to +2. Simple and practicable analytic expressions were developed for evaluating the activation energy, order of kinetics and the temperature index of the frequency factor. The activation energies obtained using method developed in this report were very accurate and closer to the input values when compared to well-known peak shape and variable heating rate methods.

Keywords: kinetic parameters; glow curves; frequency factor; thermo stimulated luminescence; dosimetry

Introduction

Thermo-stimulated luminescence (TSL) is a luminescence phenomenon peculiar to insulators and semi-conductors (Bos, 2007). The luminescence is observed when solid (phosphor) which previously had absorbed energy from radiation is heated at a constant rate (β). In principle, the exposure to radiation liberates electrons and holes which are eventually trapped within the forbidden band gap between the valence and conduction band of the crystal lattice of the phosphor. When the phosphor is heated the electron and holes recombine to produce light quanta. The intensity of the light produced during the heating process is proportional to the radiation dosage. Consequently, TSL has been widely used among others: to record radiation history of archaeological materials, in radiation dosimetry, in the study of crystal defects (Chen & Mckeever, 1997), and also in the detection of phase transition (Townsend, Maghrabi, & Yang, 2007).

The plot of the TSL light output as a function of temperature gives the glow curve. The size and position of the glow curve provide information about the trapping parameters. These parameters are characteristic of the electron traps created by the radiation. The mechanism of trapping and recombination of the resultant electrons and holes are discussed in detail by Chen and Mckeever (1997). Determination of the trapping (kinetic) parameters is crucial in many application of TSL. The major parameters which are mostly evaluated are: the activation energy (trap depth) 'E', order of kinetics 'b', frequency factor 's' and initial concentration of trapped electrons n_0. Owing to their importance, evaluation of these parameters has become an active area of research. Consequently, many models, empirical expressions and algorithm have been developed for obtaining them for the past six decades. Many of these methods have been discussed extensively by Furetta (2003). Notable among them are the initial rise (IR), variable heating rate (VHR), peak shape (PS) method and recently the three points method (Rasheedy, 2005) and two point method (Ogundare, & Chithambo, 2006a). All of these methods and expressions are mostly applicable to single peak or highly isolated glow curves and were developed on the assumption that frequency factor 's' remain a constant throughout the entire TL process. However 's' does depend on temperature according to the equation (Keating, 1961): $s(T) = sT^{\alpha}$ where $-2 \leq \alpha \leq 2$.

Here 'a' is the temperature index of the frequency factor. Ignoring this dependence, results in significant errors in evaluated kinetic parameters (Yazici, & Ozturk, 1998) depending on the value of 'a'. (Aramu, Brovetto, & Rucci, 1966) showed that when): $s(T) = sT^a$, the 'E' evaluated using the IR method and by extension the PS and VHR methods (Chen, & Mckeever, 1997) are overestimated by a factor of 'akT_m', with k being the Boltzmann constant and T_m the peak temperature of the TL glow curve. They have thus suggested that where the value of 'a' is known, the error can be corrected. Other authors (most of which have been reviewed by Furetta (2003) have developed expressions for the evaluation of 'E' as a function of 'a', but fail to suggest a reliable method of obtaining the temperature index. A simple and practical way of obtaining the index is thus crucial to accurate determination of E and other kinetic parameters. Lately, Yazici (1998) developed a method based on two heating rates and peak parameters for evaluating the index. the result of the method when applied to first order kinetics was very successful but could not be independently verified for other orders of kinetics as it requires some predetermined constants which may not necessarily be a constant throughout the entire TL process.

In this work we propose a simple and reliable method for obtaining the temperature index 'a', 'E' and 'b' for the case when: $(T) = sT^a$. The evaluated temperature index could be used with existing methods for the correction of E in expressions where the temperature dependency of s is ignored. It is also expected that 'E' evaluated by method suggested in this article would be void of errors when compared to those obtained using the well known PS and VHR methods.

Glow curve simulation

The equation governing the TL processes have been given for first and general order by Randall and Wilkins (1945); and May and Partridge)1964 respectively as:

$$I(t) = -\frac{dn}{dt} = ns\ exp(-\frac{E}{kT}) \quad (1)$$

$$I(t) = -\frac{dn}{dt} = n^b s' \exp\left(-\frac{E}{kT}\right) \quad (2)$$

Where, k is the Boltzmann constant (eV/K), t is time (s), T is temperature in (K), s the frequency factor (s^{-1}) and s' the pre-exponential factor (Rasheedy (1993); Ogundare & Chittambo (2006). The solutions to equations (1) and (2) assuming a linear heating rate (β) such that

$$T = T_0 + \beta t \quad (3)$$

where T_0, is the initial temperature of the phosphor prior heating and T the temperature at a later time are:

$$I(T) = n_0 s \exp\left(-\frac{E}{kT}\right) \exp\left[-{}^{s}/_{\beta} \int_{T_0}^{T} \exp\left(-\frac{E}{kT}\right) dT\right] \quad (4)$$

$$I(T) = n_0^b s' \exp\left(-\frac{E}{kT}\right) \left[1 + \frac{s'(b-1)n_0^{b-1}}{\beta} \int_{T_0}^{T} \exp\left(-\frac{E}{kT}\right)\right]^{-\frac{b}{b-1}} \quad (5)$$

Considering the case $s = s(a,T) = sT^a$ and consequently $s' = s'(a,T) = s'T^a$ equations (1), (2), (4) and (5) becomes:

$$I(T) = -\frac{dn}{dT} = \frac{nsT^a}{\beta}\ exp(-\frac{E}{kT}) \quad (6)$$

$$I(T) = -\frac{dn}{dT} = \frac{n^b s' T^a}{\beta} \exp\left(-\frac{E}{kT}\right) \quad (7)$$

$$I(T) = n_0 s T^a \exp\left(-\frac{E}{kT}\right) \exp\left[-\frac{s}{\beta}\varphi\right] \quad (8)$$

$$I(T) = n_0^b s' \mathrm{T}^a \exp\left(-\frac{E}{kT}\right)\left[1 + \frac{s'(b-1)n_0^{b-1}}{\beta}\varphi\right]^{-\frac{b}{b-1}} \quad (9)$$

Where φ in equation (8) and (9) is the integral:

$$\varphi = \int_{T_0}^{T} T^a \exp\left(-E/_{kT}\right) dT \quad (10)$$

φ is a complex integral and can be solved using incomplete gamma function [8].

$$\varphi = \int_{T_0}^{T} T^a \exp\left(-E/_{kT}\right) dT = \left[\frac{E}{k}\right]^{a+1} [\Gamma(-1-a,x) - \Gamma(-1-a,x_0)] \quad (11)$$

Where, $x = \frac{E}{kT}$, and $x_0 = \frac{E}{kT_0}$

Assuming as $\rightarrow 0$, $T_0 \rightarrow 0$ and $\Gamma(-1-a,x_0) \approx 0$ thus

For positive and negative integer values of a except $a = -2$

$$\varphi = \left[\frac{E}{k}\right]^{a+1} \Gamma(-1-a,x) = \left[\frac{E}{k}\right]^{a+1} \left[\frac{\mathrm{E}_i(x)}{x^{a+1}}\right] \quad (12)$$

$$\mathrm{E}_i(\mathrm{x}) = \frac{1}{x}\exp(-\mathrm{x})[1 - \mathrm{x}^{-1} + 2\mathrm{x}^{-2}] \quad (13)$$

Higher order of x have been ignored in the above equation (13) since the quantity x is always very small in the range of occurrence of TL peaks [15]. Consequently,

$$\varphi = \frac{kT^{a+2}}{E}\exp\left(-\frac{E}{kT}\right)\left[1 - \frac{kT}{E} + 2\left(\frac{kT}{E}\right)^2\right] \quad (14)$$

Equations (8) and (9) can now be written as:

$$I(T) = n_0 s T^a \exp\left(-\frac{E}{kT}\right)\exp\left(-\frac{skT^{a+2}}{\beta E}\exp\left(-\frac{E}{kT}\right)\left[1 - \frac{kT}{E} + 2\left(\frac{kT}{E}\right)^2\right]\right) \quad (15)$$

$$I(T) = n_0^b s' \mathrm{T}^a \exp\left(-\frac{E}{kT}\right)\left[1 + \frac{s'(b-1)n_0^{b-1}kT^{a+2}}{\beta E}\exp\left(-\frac{E}{kT}\right)\left[1 - \frac{kT}{E} + 2\left(\frac{kT}{E}\right)^2\right]\right]^{-\frac{b}{b-1}} \quad (16)$$

Equations (15) and (16) were used to generate computerize first and general order glow curves for the parameters: E= 0.9; a=-1, 0, 1, and 2, $\beta = 1\ K/s$, s =2.00 x 10^{13} ; $n = 1$,and kinetic order b varied from 1 to 2 in steps of 0.1.

Evaluation of kinetic parameters

Order of kinetic

To evaluate the order of kinetic, we consider equation (7) on two glow curves for β_1 and β_2 respectively at a temperature T:

$$I_{\beta 1}(T) = \frac{n_{\beta_1}^b s' T^a \exp\left(-\frac{E}{kT}\right)}{\beta_1} \quad (17)$$

$$I_{\beta 2}(T) = \frac{n_{\beta_2}^b s' T^a \left(-\frac{E}{kT}\right)}{\beta 2} \quad (18)$$

Where $n_{\beta i}(T)$ is the area under the glow curve from temperature T to the end of the glow curve. Dividing equation (17) by (18) and rearranging,

$$b = \frac{\ln\left[\frac{\beta_2 I_{\beta_1}(T)}{\beta_2 I_{\beta_2}(T)}\right]}{\ln\left[\frac{n_{\beta_1}(T)}{n_{\beta_2}(T)}\right]} \quad (19)$$

Determination of 'E' and 'a'

Evaluation of the activation energy and temperature dependent index involves the consideration of one of the glow curves used in the evaluation of b. Three points on the glow curve at a heating rate β is given according to equation (7) as:

$$I_1(T_1) = \frac{n_0^b s' T_1^a}{\beta} \exp\left(-\frac{E}{kT_1}\right) \quad (20)$$

$$I_2(T_2) = \frac{n_0^b s' T_2^a}{\beta} \exp\left(-\frac{E}{kT_2}\right) \quad (21)$$

$$I_3(T_3) = \frac{n_0^b s' T_3^a}{\beta} \exp\left(-\frac{E}{kT_3}\right) \quad (22)$$

Dividing equations (20) by (21) and (23) separately and rearranging we obtain two equations that can be solved simultaneously:

$$ax_{12} + Ey_{12} = z_{12} \quad (23)$$

$$ax_{13} + Ey_{13} = z_{13} \quad (24)$$

Where $x_{ij} = ln\left(\frac{T_i}{T_j}\right)$; $y_{ij} = \frac{1}{k}\left(\frac{1}{T_j} - \frac{1}{T_i}\right)$; and $z_{ij} = ln\left[\left(\frac{I_i}{I_j}\right)\left(\frac{n_j}{n_i}\right)^b\right]$.

If b obtained in equation (19) is used then equations (23) and (24) can be used to evaluate the activation energy E and the temperature index (a) of the frequency factor.

Results and Discussion

A total of 44 glow curves were theoretically generated in MATLAB (MATLAB R2007a, The MathWorks Inc., 3 Apple Hill Drive, Natick, MA 01760) environment using equations (15) and (16) for the various values of 'a' and 'b' considered. Fig.1 is a sample of one of the glow curves for a=-1 and b=1.4. Generally, the behavior of the glow curves with respect to variation in input parameters E, b, and n_0 are similar to those for which s is temperature independent (Bos, 2001).

Many of the methods available in literature for the evaluation of E require the prior knowledge of b. In some case the shape and shift of peak intensities are used to predict b while in other cases the peak parameters are used for the evaluation of b. An expression for the evaluation of b for the case s (T) is scanty in literature. In this communication, we evaluate b using equation (19) for β =1 and 5 K/s. This equation was applied at various portions of the entire glow curves starting from the initial rise region. It was observed that the value of b obtained at the initial rise region was accurate when intensities within 10% of maximum intensities (I_m) were used only for order one. For higher orders, the most accurate b was found when intensities within 10% of I_m at the descending region of the glow curves were used. The values of b obtained at this region are given for in table 1 all input values of "a" and b considered in table1. The inaccuracy obtained at the initial rise region for all b except for b=1 could be due to the fact that at the initial rise region, b is about one (Ogundare & Chithambo (2006b). Furthermore, since b is a measure of re-trapping probability, at the initial rise region where re-trapping is negligible (Sunta, Feria, & Chubaci, 2005)), values of b evaluated at this region is expected to be inaccurate for b >1. It is worthy of note that equation (19) is similar to that obtained by Ogundare and Chithambo (2006a) although they did not consider the temperature dependency of s. The implication of this is that the equation is very valid for b irrespective of the temperature dependence of s and can thus be used for general glow curves. The values of b obtained in table 1 are very accurate for all values of 'a' and b except at a=0, 1 and 2 for input b=1 where there were negligible error of about 1%.

The values of the temperature index 'a' and activation energy 'E' obtained from equations (23) and (24) are given in table 2 and 3 respectively. It is obvious from the formulae that

the value of the kinetic order is required for evaluating the two parameters. The calculated values of the kinetic order in tab. 1, were used in the evaluations. Just as the case of the kinetic order, the accuracy of equations 23 and 24 were tested in different portions of the glow peak. At the descending part of the peak, the most accurate values of "a" and "E" had about 10% error in some cases, while on picking the three points from a mixture of ascending and descending point also yield considerable errors. The best result was obtained when the points are selected at the initial rise region of the peak within 10% of peak intensity. The result obtained for this region is thus presented on tab. 2 and 3. The values of the temperature index were very accurate and to the best of our knowledge we present for the first time a simple method for evaluating "a" for general order kinetics. The value of a, thus obtained could be used for correcting activation energy obtained using methods such as the IR (Aramu, Brovetto, & Rucci, 1966). The activation energy obtained from equations 23 and 24 should be free of errors introduced by neglecting the temperature dependency of "s". A possible source of error however could arise in reading the point on the glow peak for evaluating the trap parameters. The error introduced by inaccurate reading points on the glow curve will vary depending on the accuracy in reading the temperature (K) and the intensities on the glow peak. A comparison between the activation energy obtained using the method highlighted in this work and those obtained using the famous Chen's (1969) PS (E_T) and Booth (1954) and Bohun (1954) VHR methods for a= -1 for various values of b considered is given in table 4. In the formulation of these two methods, "a" was assumed to be zero; this could be responsible for the various errors in the evaluated E for the different b considered. Although both methods give fairly accurate results, the result obtained using the method introduced in this article is of better accuracy.

Conclusion

Most of the methods available for analyzing TL glow curves were formulated with the assumption that the frequency factor is temperature independent. This has led to considerable error in evaluated trap parameters in some cases. In order to obtain more accurate trap parameters, the temperature dependency of the frequency factor is considered in this work. A simple and practical way of determining the temperature index, order of kinetics and activation energy with better accuracy is introduced. It is however acknowledged that the algorithm suggested for the evaluation of trap parameters in this article, like most methods before it, is applicable to single and well isolated glow peaks. We therefore suggest that for this method to be applicable for multiple peaks glow curve, experimental procedures such as thermal treatment (Pagonis and Shannon, 2000) are applied for isolating the peaks before this method becomes applicable. It should also be mentioned that where computerize glow curve fitting is applied to multiple peak glow curve, the temperature index of the frequency factor can be considered as one of the fitting parameters.

Table 1: Values of the kinetic order obtained using equation (19) for various Input values of "a" and "b"

Input b	Calculated b			
	a=-1	a=0	a=1	a=2
1.00	1.000	1.010	1.010	1.010
1.10	1.100	1.100	1.100	1.100
1.20	1.200	1.200	1.200	1.200
1.30	1.300	1.300	1.300	1.300
1.40	1.400	1.400	1.400	1.400
1.50	1.500	1.500	1.500	1.500
1.60	1.600	1.600	1.600	1.600
1.70	1.700	1.700	1.700	1.700

1.80	1.800	1.800	1.800	1.800
1.90	1.900	1.900	1.900	1.900
2.00	2.000	2.000	2.000	2.000

Table 2: Values of temperature dependent index (a) obtained using equation 23 and 24 at various values of b

Input a	Calculated a										
	1.0	1.1	1.2	1.3	1.4	1.5	1.6	1.7	1.8	1.9	2.0
-	-	-	-	-	-	-	-	-	-	-	-
1.000	1.000	1.000	0.916	1.001	1.000	1.000	1.000	1.000	1.000	1.000	1.000
0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.002	1.000	1.000
2.000	2.000	2.000	2.000	2.000	1.822	2.000	2.000	2.000	2.000	2.000	2.000

Table 3: Values of activation energy using equations 23 and 24.

B	Calculated E			
	a= -1	a=0	a= 1	a=2
1.0	0.900	0.900	0.900	0.853
1.1	0.900	0.900	0.900	0.900
1.2	0.899	0.900	0.900	0.900
1.3	0.900	0.900	0.900	0.900
1.4	0.900	0.900	0.900	0.902
1.5	0.900	0.900	0.900	0.900
1.6	0.900	0.900	0.900	0.900
1.7	0.900	0.900	0.900	0.900
1.8	0.900	0.900	0.900	0.900
1.9	0.900	0.900	0.900	0.900
2.0	0.900	0.900	0.900	0.900

Table 4: Comparison of the activation energy E obtained using PS, VHR and that obtained from equations 23 and 24 at a=-1.

	E		
b	**PS Chen(1969)**	**VHR (Booth,1954;Bohun, 1954)**	**This work Equations 23 and 24**
1.0	0.865	0.869	0.900
1.1	0.854	0.887	0.900
1.2	0.909	0.865	0.899
1.3	0.943	0.825	0.900
1.4	0.971	0.906	0.900

1.5	0.851	0.972	0.900
1.6	0.882	0.959	0.900
1.7	1.090	0.833	0.900
1.8	1.020	0.853	0.900
1.9	0.976	0.911	0.900
2.0	0.975	0.814	0.900

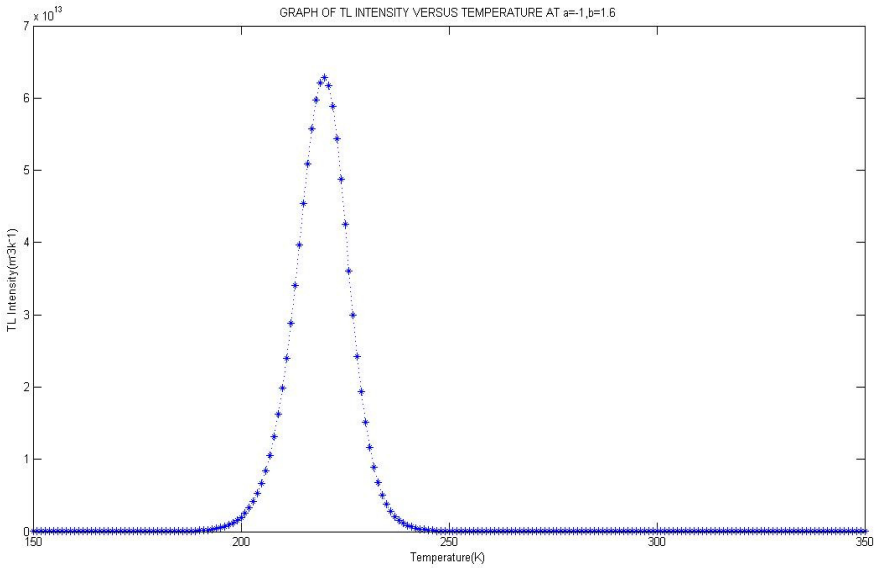

Fig.1: Simulated glow curve using equation (16) for a=-1 and b=1.4.

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