

Evaluation of kinetic parameters of traps in thermoluminescence phosphors

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Abstract

A method for evaluating trap depth E , order of kinetics b and frequency factor s from a thermoluminescence (TL) glow peak has been developed. The method is based on using intensities and temperatures at any three points on the glow peak. Unlike similar techniques that provide no expression for frequency factor, the present formulation provides such an expression. The expression does not require knowledge of the temperature at which maximum intensity occurs, a parameter not usually known accurately from experimental glow peak data. For the method, it is found that use of points in the ascending part of the glow peak where the intensities are less than 10% maximum intensity gives parameter values closest to the true ones. Possible reasons for getting less accurate results when points are taken beyond this region are discussed. Values of the activation energy calculated using the present technique were always close to the true value. However, the frequency factor only approaches the true value as the dose given to the sample approaches saturation. When the three data points are selected in the initial-rise region, the equation for evaluating E in the method described in this paper becomes a two-point version of the initial-rise method. The advantage of the present technique over the initial-rise method is that it also gives b and hence s . The method is used to analyse the TL glow curve of a gamma-irradiated sample from Ijero-Ekiti, Nigeria.

1. Introduction

Thermoluminescence (TL) phosphors generally exhibit glow curves with one or more peaks when the charge carriers are released. The glow curve is characteristic of the different trap levels that lie in the band gap of the material. The traps are characterized by certain physical parameters that include trap depth (E) and frequency factor (s).

For many TL applications, a clear knowledge of these physical parameters is essential. In the study of relatively deep trapping defect-states in various solid state materials as well as TL dating, a detailed analysis of TL glow curves is indispensable. In order to obtain these physical parameters, one needs to fit the glow curve data to a TL model that best describes the TL intensity as a function of these parameters. The widely used TL models are first-order (Randall and Wilkins, 1945), second-order (Garlick and Gibson, 1948) and the general-order (GO) (May and Partridge, 1964) kinetics models. Chen and Mckeever (1997) have reviewed some of these methods and discussed their advantages and disadvantages.

In this work, expressions are developed for the estimation of parameters including trap depth E , order of kinetics b and the frequency factor s . We investigated the dependence of the accuracy of the parameters calculated on the region of the glow peak from where the three points are selected. We then suggest the best region of the glow peak where the three points can be selected for most reliable results.

2. The new technique

The technique is based on the GO model (Rasheedy, 2005) given by Eq. (1).

$$I(t) = -\frac{dn}{dt} = \frac{n^b}{N^{b-1}} S \exp(-E/kT), \quad (1)$$

where N is the concentration of the total traps and n is the concentration of filled traps at temperature T .

At a temperature T_i , Eq. (1) becomes

$$\begin{aligned} I_i &= n_i^b S' \exp(-E/kT_i) = \left(\frac{n_i}{n_e}\right)^b S' n_e \exp(E/kT) \\ &= (n_{ie})^b n_e s \exp(-E/kT_i), \end{aligned} \quad (2)$$

where $S' = S/N^{b-1}$, $s = S' n_e^{b-1} = S(n_e/N)^{b-1}$ and $n_{ie} = n_i/n_e$. n_e , which is introduced in order to ensure that the frequency factor has a unit of s^{-1} , is the area from a temperature T_e on the glow peak to the end of the glow peak. T_e can be chosen at any point in the initial-rise region of a glow peak. However, whenever possible (i.e. when there is no peak overlap), n_e should be taken as the area under the whole glow peak. n_i is the area under the glow peak from T_i to the end of the glow peak.

Three equations are obtained when i in Eq. (2) is replaced by 1, 2, 3. On re-arrangement, the equations are

$$\frac{kT_1}{E} \ln \left(\frac{n_{1e}^b n_e s}{I_1} \right) = 1, \quad (3a)$$

$$\frac{kT_2}{E} \ln \left(\frac{n_{2e}^b n_e s}{I_2} \right) = 1, \quad (3b)$$

$$\frac{kT_3}{E} \ln \left(\frac{n_{3e}^b n_e s}{I_3} \right) = 1. \quad (3c)$$

Eq. (3a) divided by Eq. (3c) gives

$$\frac{T_1 \ln(n_{1e}^b n_e s / I_1)}{T_3 \ln(n_{3e}^b n_e s / I_3)} = 1 \quad (4a)$$

and Eq. (3b) divided by Eq. (3c) gives

$$\frac{T_2 \ln(n_{2e}^b n_e s / I_2)}{T_3 \ln(n_{3e}^b n_e s / I_3)} = 1. \quad (4b)$$

By making the following substitutions, $\gamma = T_1/T_3$, $\alpha = T_2/T_3$, $\delta = n_e s$, Eq. (4a) becomes

$$b \ln \frac{n_{1e}^\gamma}{n_{3e}} + \ln \delta^{\gamma-1} - \ln \frac{I_1^\gamma}{I_3} = 0 \quad (5a)$$

and Eq. (4b) becomes

$$b \ln \frac{n_{2e}^\alpha}{n_{3e}^\alpha} + \ln \delta^{\alpha-1} - \ln \frac{I_2^\alpha}{I_3^\alpha} = 0. \quad (5b)$$

Multiplying Eq. (5b) by $1/(\alpha-1)$ and subtracting the result from Eq. (5a) times $1/(\gamma-1)$ gives an expression for calculating the order of kinetics, b as

$$b = \frac{\frac{\ln(I_1^\gamma/I_3)}{\gamma-1} - \frac{\ln(I_2^\alpha/I_3)}{\alpha-1}}{\frac{\ln(n_{1e}^\gamma/n_{3e})}{\gamma-1} - \frac{\ln(n_{2e}^\alpha/n_{3e})}{\alpha-1}}. \quad (6)$$

An expression for calculating E is obtained using any two of equations (3a)–(3c). For instance, using Eqs. (3b) and (3c) the expression for E is obtained to be

$$E = \frac{k \ln\{(n_{2e}/n_{3e})^b I_3/I_2\}}{(1/T_2 - 1/T_3)}. \quad (7)$$

From Eq. (2) the frequency factor s can then be obtained as

$$s = \frac{I_i \exp(E/kT_i)}{(n_{ie})^b n_e}. \quad (8)$$

To use Eq. (8), T_i may be taken to be the lowest of the three temperatures selected for the analysis.

3. Validation of the technique

The glow peaks used for the validation, that is, test and verification of the method, were generated from a model which assumes the presence of one active trap (AT), one thermally disconnected deeper trap (TDDT) and one recombination centre (RC). This model is well described by Sunta et al.(1999). The differential equations that describe the charge transfer processes in this model are

$$\frac{dn}{dt} = -ns \exp\left(-\frac{E}{kT}\right) + n_c(N-n)A_n, \quad (9)$$

$$\frac{dm}{dt} = n_c(M-m)A_m, \quad (10)$$

$$\begin{aligned} \frac{dn_c}{dt} = & ns \exp\left(-\frac{E}{kT}\right) - n_c(N-n)A_n \\ & - n_c(M-m)A_m - n_c(m+n+n_c)A_h \end{aligned} \quad (11)$$

and the TL intensity is calculated by

$$I = n_c(m+n+n_c)A_h, \quad (12)$$

where M and m are the concentrations of the total and the filled TDDTs, respectively, and A_m is the capture coefficient of the TDDTs. N and n are the concentrations of the total and the filled traps respectively and n_c that of the free carriers. E and s are the activation energy and the frequency factor of the traps, respectively. A_n and A_h are the capture coefficients of the traps and the recombination centres (RC), respectively. Eight glow peaks were simulated with this model. The input parameters for glow peaks 1 and 2 are taken from the work of Sunta et al. (1999), glow peak 3 from Sunta et al. (2001) and glow peaks 4 to 8 from Sunta et al. (2002). These parameters are listed in Table 1.

Table 1.

Parameters used for the numerical glow peaks calculations (heating rate used is 1 K s^{-1})

Peak No.	$N \text{ (cm}^{-3}\text{)}$	$M \text{ (cm}^{-3}\text{)}$	$n_0 \text{ (cm}^{-3}\text{)}$	$m_0 \text{ (cm}^{-3}\text{)}$	$A_n \text{ (cm}^3 \text{ s}^{-1}\text{)}$	$A_m \text{ (cm}^3 \text{ s}^{-1}\text{)}$	$A_h \text{ (cm}^3 \text{ s}^{-1}\text{)}$	$E \text{ (eV)}$	$s \text{ (s}^{-1}\text{)}$
1.	10^{10}	10^{10}	10^{10}	10^{10}	10^{-7}	10^{-5}	10^{-5}	1.0	10^{12}
2.	10^{10}	10^{10}	10^{10}	10^{10}	10^{-7}	10^{-6}	10^{-6}	1.0	10^{12}
3.	10^{18}	10^{22}	10^{16}	10^{20}	10^{-18}	10^{-18}	10^{-18}	1.0	10^7
4.	10^{12}	10^{13}	10^{11}	10^{12}	10^{-7}	10^{-7}	10^{-7}	1.0	10^{12}
5.	10^{12}	10^{10}	10^{11}	10^9	10^{-7}	10^{-7}	10^{-7}	1.0	10^{12}
6.	10^{12}	10^{12}	3.94×10^{11}	9.93×10^{11}	10^{-7}	10^{-6}	10^{-7}	1.0	10^{12}
7.	10^{12}	10^{12}	5.0×10^{11}	6.7×10^{10}	10^{-7}	10^{-8}	10^{-7}	1.0	10^{12}
8.	10^{12}	10^{12}	10^{10}	10^9	10^{-7}	10^{-8}	10^{-6}	1.0	10^{12}

The present technique and the first-order kinetic deconvolution function of Kitis et al. (1998) were also used to analyse the experimental glow curve of a muscovite sample from Ijero-Ekiti, Nigeria. The glow curve was obtained from the sample annealed at $400 \text{ }^\circ\text{C}$.

4. Results and discussion

The kinetics parameters calculated using Eqs. (6)–(8) on the glow peaks numerically generated using the parameters in Table 1 are presented in Table 2. Three approaches, labeled as approach I, II and III, were used to select three points on a particular glow peak to be analysed. Approach I; II; and III involves selecting the three points at temperatures T_a , $(T_a - 10)$ and $(T_a - 20) \text{ K}$; $(T_m - 10)$, T_m and $(T_m + 10) \text{ K}$; and T_d , $(T_d - 10)$ and $(T_d - 20) \text{ K}$, respectively. In this case, T_m is the temperature at maximum intensity and T_a and T_d are the temperatures at one-tenth maximum intensity on the ascending and descending part of the glow peak, respectively. Table 2 shows that the values of E and s obtained using approach I are in very good agreement with the true values. These results obtained, with approach I, are found to be better than those from GO glow curve fitting as reported by Sunta et al. (2002) for glow peaks 4 to 8.

Table 2.

Parameters obtained from analysing glow peaks obtained with parameters in Table 1

		Peak No.							
		1	2	3	4	5	6	7	8
	<i>E</i>	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000
Approach	<i>s</i>	1.0×10^{12}	1.0×10^{12}	1.0×10^7	9.2×10^{11}	1.1×10^{11}	6.8×10^{11}	6.2×10^{11}	2.0×10^{11}
I	<i>b</i>	1.05	1.10	1.02	1.06	1.99	1.29	1.74	1.32
	<i>E</i>	0.995	0.978	0.998	0.993	0.917	0.908	0.845	0.912
Approach	<i>s</i>	8.4×10^{11}	5.0×10^{11}	9.7×10^6	7.5×10^{11}	9.0×10^9	3.8×10^{10}	4.8×10^{10}	1.4×10^{10}
II	<i>b</i>	1.04	1.05	1.01	1.04	1.70	1.05	1.26	1.07
	<i>E</i>	0.933	0.938	0.987	0.935	0.623	0.941	0.924	0.948
Approach	<i>s</i>	1.4×10^{11}	1.5×10^{11}	7.8×10^6	1.3×10^{11}	6.7×10^5	9.2×10^{10}	2.5×10^{10}	3.4×10^{10}
III	<i>b</i>	1.02	1.02	1.01	1.02	0.96	1.02	1.02	1.02

As shown in Table 2, less accurate values are obtained when approaches II and III are used. In fact in some cases, as shown for glow peak 5 for approach III and glow peak 7 for approach II, values that differ significantly from the true values are obtained. The results obtained using a similar method proposed by Rasheedy (2005) showed a similar trend. One concludes then that it is not in all cases that three points chosen on any part of the glow peak will give reasonably accurate results as suggested in Rasheedy (2005). We therefore suggest that when using the technique presented in this paper or similar ones, the points to be used for the analysis should be taken in the initial-rise region (where intensities are less than 10% maximum intensity) of the peak if this part does not overlap with another peak. Otherwise an overlap removal procedure (e.g. thermal cleaning) should be applied. There are several reasons for the reduction in accuracy when points are selected beyond initial-rise region. Firstly, the further away from the initial-rise region one is, assumptions such as quasi-equilibrium on which the derivation of Eq. (1) is based become unrealistic. For example quasi-equilibrium is known to be well satisfied on the low temperature side of a glow peak rather than on the high-temperature side (Sunta et al., 2001). Furthermore if more than one trap and one recombination centre are present in a material the performance of methods based on Eq. (1) which is based on a model of one trap and one recombination centre become questionable. However, in the initial-rise region of a given glow peak, the influence of the other traps is negligible. Therefore, any method using the initial-rise region is expected to give more accurate results. The above reasons may account for why the results of fitting done in Sunta et al. (2002) are less accurate than the results from the present technique. In his fitting he made use of all the points including those where QE may be less satisfied.

The frequency factors calculated using the expression in Eq. (8), as shown in Table 2, are also close to the true values. Eq. (8) is not an approximation unlike the commonly used expression (Chen and Mckeever, 1997) for frequency factor calculation. In addition, the use of the present expression does not require knowledge of T_m , a parameter that one may not know accurately from experimental data of a glow peak.

As shown in Table 3, using approach I, while for all n_0/N the exact value of activation energy was reproduced, the exact value of the frequency factor is approached as n_0/N approaches 1. The glow

peaks in Table 3 are selected from glow peaks in Table 1 with the exception of OTOR glow peak generated from a model of one-trap one recombination centre (OTOR). The OTOR model is also as shown in Fig. 1 but without a TDDT. Table 3 shows that for both models, the frequency factor approaches very closely the true value as n_0/N approaches 1. Therefore, in order to obtain parameters that are very close to the true values from a glow peak using this technique and similar ones, TL glow curve should be obtained from a sample irradiated to a high dose (if possible to a dose near saturation).

Table 3.

Parameters calculated using approach I for various values of n_0/N . n_0 is varied to obtain the desired value of n_0/N

Peak No.	Parameter	$n_0/N=0.01$	$n_0/N=0.1$	$n_0/N=1.0$
	E	1.000	1.000	1.000
3	s	1.0×10^7	1.0×10^7	1.0×10^7
	b	1.02	1.02	1.02
	E	1.000	1.000	1.000
5	s	2.0×10^{10}	1.1×10^{11}	1.0×10^{12}
	b	1.55	1.99	2.09
	E	1.000	1.000	1.000
8	s	2.0×10^{11}	6.1×10^{11}	1.0×10^{12}
	b	1.32	1.43	1.14
	E	1.000	1.000	1.000
OTOR	s	5.0×10^{11}	9.2×10^{11}	1.0×10^{12}
	b	1.58	1.15	1.06

The input parameters used to generate the OTOR peak are $E = 1 \text{ eV}$, $s = 10^{12} \text{ s}^{-1}$, $N = 10^{10} \text{ cm}^{-3}$, $A_n = 10^{-7} \text{ cm}^3 \text{ s}^{-1}$, $A_h = 10^{-5} \text{ cm}^3 \text{ s}^{-1}$.

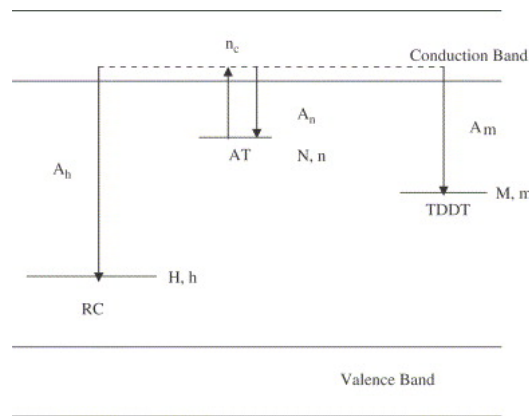


Fig. 1. Energy levels of the scheme used to generate the numerical glow peaks.

Using approach I as discussed in this work, since in the initial rise region $n_2 \cong n_3 \cong n_0$ (Chen and Mckeever, 1997), Eq. (7) becomes independent of b and hence can be considered to be a two-point version of the initial rise method for evaluating E . The E values calculated using Eq. (7) will then be very similar to those from initial-rise method. The advantage of the present technique over the initial-rise method is that in addition to E , b can be calculated using Eq. (6) and hence s using Eq. (8).

The activation energy of the experimental glow peak of a muscovite sample (Fig. 2) calculated using the present technique and the first-order deconvolution function of Kitis et al. (1998) are 0.835 ± 0.101 and 0.830 eV, respectively. The frequency factor were calculated to be $(1.01 \pm 0.31) \times 10^7$ and $4.56 \times 10^7 \text{ s}^{-1}$, respectively. First order kinetics was assumed because glow curves of the sample irradiated to different doses showed that the position of the peak did not change with change in dose. There is a good agreement between parameters calculated using the two methods. The agreement again confirms the applicability of the present technique for glow peak analysis.

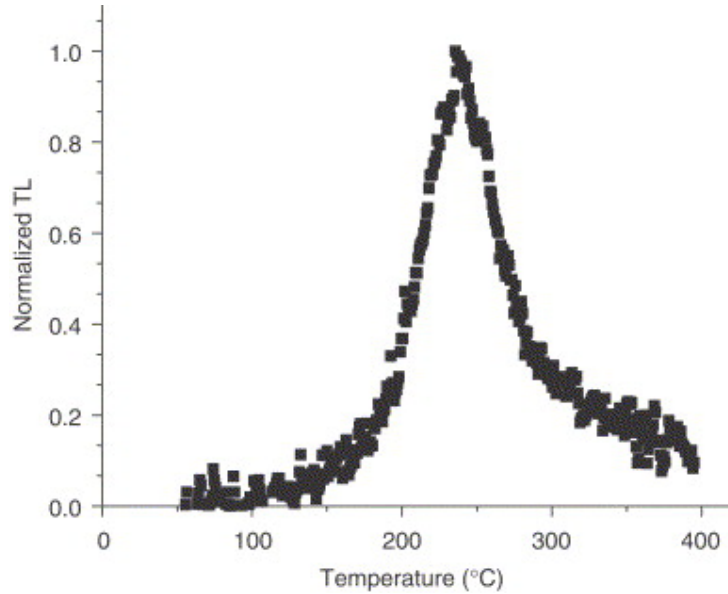


Fig. 2. Experimental glow curve of muscovite sample irradiated to a gamma dose of 8.5 kGy and readout at a heating rate of $8 \text{ }^\circ\text{C s}^{-1}$.

5. Conclusion

A new method for estimating TL kinetic parameters E , b and s has been developed. To use this method the intensities and temperatures at three points taken from the ascending part of the glow peak (where possible in the region where intensities are less than 10% I_m) should be used. Glow curves for analysis using this technique should preferably be obtained from the phosphor irradiated to a very high dose. Kinetic parameters calculated from an experimental glow peak using the technique are comparable to the ones obtained using a deconvolution method.

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