On the thermoluminescence glow curve analysis recorded under hyperbolic heating profile

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Abstract

In the present paper we have analysed thermoluminescence peaks recorded under hyperbolic heating scheme by considering numerically computed resulting from (i) general order kinetics model, (ii) one trap one recombination centre model and (iii) interactive multitrap system model. We have observed that in the models, the peak temperature shifts with the filling ratio. For the general order kinetics model, the peak shape method leads to the almost accurate value of activation energy for saturated glow peaks whereas the other two models yield appreciable errors.

Keywords: thermoluminescence, activation energy, order of kinetics, peak shape method.

1.0 INTRODUCTION

Thermoluminescence (TL) is observed when in the process of irradiating a material, a part of the irradiation energy is used to transfer electrons from the valence band to the traps lying within the band gap. This energy stored in the trapped electrons is released by raising the temperature of the material and the released energy is manifested as luminescence. The trapping process and the subsequent luminescence find important application in ionizing radiation dosimetry and in the observation of long persistent phosphors. Much information about the trapping process and the release of the trapped electrons is obtained from TL spectra in which TL intensity is monitored under a controlled heating scheme [1,2] after turning off the irradiating source. Usually a linear heating scheme is used to record TL, but sometimes hyperbolic heating scheme which is an important adjunct of linear heating scheme is also adopted to check the reliability [3] of the values of the trapping parameters i.e. the activation energy E, frequency factor s and the order of kinetics b [1,2]. Although a number of glow curves have been analysed by kinetics order approach, some anomalous results have been reported by different groups [4-7]. So one has to go beyond the general order of kinetics (GOK) model for rigorous analysis of TL glow curves. Two such models are : (i) one-trap-one-recombination (OTOR) model [8] and (ii) interactive multitrap system (IMTS) model [8]. Both these models are based on the band picture of solids [9]. IMTS model incorporates the effects of thermally disconnected deep traps (TDDT) the importance of which have been discussed by Fain et al. [10, 11].

In the present paper we analyse the unsaturated TL peaks recorded under hyperbolic heating scheme by using GOK, OTOR and IMTS models. The unsaturated TL peaks correspond to the values of the filling ratio \( f = \left( \frac{n_0}{N} \right) \) less than unity where \( n_0 \) is the initial concentration of trapped electrons and \( N \) is the concentration of electron traps. For saturated TL peaks, \( f = 1 \). The analysis of unsaturated TL
peaks is very much important from the point of view of the applications of TL in radiation measurements and dosimetry [1,2]. Singh [12] has shown that for non-first order unsaturated TL peaks recorded with linear heating scheme peak temperature (Tm) shifts with change in order unsaturated TL peaks recorded with linear heating dosimetry [1,2]. The validity of peak shape method for unsaturated TL peaks has been critically examined under hyperbolic heating scheme.

2.0 METHODOLOGY

The basic set of coupled differential equations for the OTOR model [8] is given by

\[ \frac{dn}{dt} = -nse^{E/kT} + n_c(N-n)A_n \]  
\[ \frac{dn_c}{dt} = nse^{E/kT} - n_c(N-n)A_n - n_c n_h A_h \]

where \( n_c, n_h \) and \( n \) are concentration of electrons in the conduction band, concentration of holes in the recombination centres and concentration of electrons in the traps respectively. \( k \) is the Boltzmann constant and \( T \) is the temperature at time \( t \). \( A_n \) and \( A_h \) are retrapping and recombination coefficients respectively. The charge neutrality condition [8] in this case is given by

\[ n_h = n + n_c \]  
(3)

The TL intensity \( I(t) \) may be written as

\[ I(t) = -\frac{dn_h}{dt} = n_h n_h A_h \]

(4)

Now, we use the quasi-equilibrium (QE) approximation [1,2] given by

\[ \frac{dn}{dt} \ll \frac{dn_c}{dt} \]  
(5)

\[ \frac{dn}{dt} \ll \frac{dn_c}{dt} \]  
(6)

These QE conditions imply that the free electron concentration in the conduction band is almost stationary. In practice, this is realized by considering \( n_c << n \), i.e.

\[ n_h \approx n \]  
(7)

The TL intensity \( I(t) \) in OTOR model takes the form

\[ I \approx \frac{dn}{dt} = nse^{E/kT} \left[ 1 - \frac{A_n(N-n)}{A_n(N-n) + n_h A_h} \right] \]  
(8)

Equation (8) is known as generalized one trap (GOT) expression [7] for TL intensity \( I(t) \). For negligible retrapping, i.e. for \( A_h \approx 0 \), this equation reduces to the well-known first order kinetics model of Randall and Wilkins [13] given by

\[ I \approx -\frac{dn}{dt} = nse^{E/kT} \]  
(9)

For equal probability of recombination and retrapping i.e.

\[ A_n = A_h \], equation (8) transforms to the well-known second order kinetics model of Garlick and Gibson [14]

\[ I \approx -\frac{dn}{dt} = \frac{n^2}{N}se^{E/kT} \]  
(10)

May and Partridge [15] suggested an equation, known as general order kinetics (GOK) equation given by

\[ I \approx -\frac{dn}{dt} = \frac{n^b}{N^{b+1}}se^{E/kT} \]

(11)

It is to be noted that equation (11) yields equations (9) and (10) for \( b = 1 \) and 2 respectively.

The hyperbolic heating scheme can be written as [16]

\[ T^{-1} = T_o^{-1} - \beta t \]

(12)

Here \( \beta \) is the heating parameter and \( T_o \) is the initial temperature. The heating rate is given by

\[ \frac{dT}{dt} = \beta T^2 \]

(13)

\( \beta \) is so chosen that at peak temperature \( T_m \), the heating rate becomes unity. TL intensities for different orders of kinetics are as follow.

For \( b = 1 \)

\[ I(T) = sNf e^{E/kT} \exp \left[ -\frac{S}{\beta} J \right] \]

(14)

For \( b = 2 \)

\[ I(T) = sNf^2 e^{E/kT} \left[ 1 + \frac{Sf}{\beta} J \right] \]

(15)

For \( b \neq 1 \)

\[ I(T) = sNf^b e^{E/kT} \left[ 1 + \frac{(b-1)sf^{b-1}J}{\beta} \right] \]

(16)

The corresponding maxima conditions are given below.

For \( b = 1 \)

\[ \frac{BE}{k} = s e^{E/kT} \]

(17)

For \( b = 2 \)

\[ \frac{BE}{k} = 2sf^2 e^{E/kT} \left[ 1 + \frac{Sf}{\beta} J \right]^{-1} \]

(18)

For \( b \neq 1 \)

\[ \frac{BE}{k} = bsf^{b-1} e^{E/kT} \left[ 1 + \frac{(b-1)sf^{b-1}J}{\beta} \right]^{-1} \]

(19)

where the temperature integral \( J \) is given by

\[ J = \int_{T_0}^{T} \frac{e^{E/kT}}{T^2} dT' = \frac{k}{E} \left[ e^{E/kT} - e^{E/kT_o} \right] \]

(20)

Under normal experimental conditions, \( T_o << T \). Therefore, the integral \( J \) can be expressed as [17]
\[ J \approx \frac{k}{E} e^{-\frac{E}{RT}} \]  
 \[(21)\]

For IMTS model, the set of coupled differential equations are [8]
\[
\frac{dn}{dt} = -nse^{\frac{E}{RT}} + N_n (N-n)A_n
\]  
 \[(22)\]
\[
\frac{dn}{dt} = nse^{\frac{E}{RT}} - n_c (N-n)A_n
\]  
 \[(23)\]
\[
\frac{dm}{dt} = n_c (M-m)A_m
\]  
 \[(24)\]

Here, the charge neutrality condition is given by [8]
\[ n_h = n + n_c + m \]
 \[(25)\]

The TL intensity in this case may be estimated using equation (4) where \( n_0 \) is to be taken from equation (25).

**Table 1:** Fitting parameters of glow curves of colourless calcite (without filter) corresponding to heating rate 3.03 Ksec\(^{-1}\).

<table>
<thead>
<tr>
<th>Order of kinetics (b)</th>
<th>Filling ratio (f)</th>
<th>Peak temperature (K)</th>
<th>( E_\omega ) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.5</td>
<td>0.1</td>
<td>398.9</td>
<td>0.998</td>
</tr>
<tr>
<td></td>
<td>0.2</td>
<td>394.5</td>
<td>0.998</td>
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<tr>
<td></td>
<td>0.4</td>
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<tr>
<td></td>
<td>0.6</td>
<td>387.7</td>
<td>0.998</td>
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<tr>
<td></td>
<td>0.8</td>
<td>385.9</td>
<td>0.998</td>
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<td></td>
<td>1.0</td>
<td>384.6</td>
<td>0.998</td>
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<td>0.1</td>
<td>414.3</td>
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<td>404.8</td>
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<tr>
<td></td>
<td>0.4</td>
<td>395.9</td>
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<td>0.6</td>
<td>390.8</td>
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<td></td>
<td>0.8</td>
<td>387.6</td>
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</tr>
<tr>
<td></td>
<td>1.0</td>
<td>384.6</td>
<td>1.0</td>
</tr>
</tbody>
</table>

**3.0 RESULTS AND DISCUSSIONS**

In table 1, we show the peak temperature \( T_m \) of unsaturated and saturated TL peaks for \( E = 1 \) eV and \( s = 10^{12} \) sec\(^{-1}\) for \( b = 1.5 \) and 2. It is seen that with increasing \( f \), \( T_m \) decreases. In this table we have also depicted the values of \( E_\omega \) using the \( \omega \)-formula of peak shape method [16]. We see that for the cases, the values of \( E_\omega \) are in excellent agreement with the input values of \( E \).

Now we consider the TL peaks resulting from OTOR and IMTS models. The sets of coupled differential equations (1-2), (22-24) are transformed from time \((t)\) to temperature \((T)\) domain by using equation (13). The new set of coupled differential equations are solved by using a modified version of the fourth order Runge-Kutta method [18]. Entire computation has been carried out in FORTRAN77 language.

Following Sunta [19], the initial values of trap occupancies \( n_0 \) and \( m_0 \) have been obtained by assuming the traps are filled up with increasing dose of radiation according to saturated exponential function. Corresponding filling constants are proportional to \( A_h \) and \( A_h \).

In tables 2 and 3, glow curves are computed for different values of \( n_0 \), \( A_h \) and \( A_h \) in OTOR model and for \( n_0 \), \( m_0 \), \( M \), \( A_h \), \( A_h \) and \( A_h \) in IMTS model. In all the cases, the values of \( E \), \( s \) and \( N \) are taken as 1 eV, \( 10^{12} \) sec\(^{-1}\) and \( 10^{12} \) cm\(^{-3}\) respectively. We have applied the \( \omega \)-formula of peak shape method [16] to these numerically computed peaks to obtain \( E_\omega \), the activation energy calculated in this method. In both the tables, we have included the proportional error \( \Delta E_\omega = \frac{E - E_\omega}{E} \times 100\% \). It is clear from tables 2 and 3 that the errors in the determination of the activation energy by peak shape method is quite high for saturated TL peaks \( (f = 1) \). Even for unsaturated TL peaks \( (f < 1) \), the error is appreciable for the case \( A_h > A_h \) i.e. in which retrapping dominates recombination. \( \Delta E_\omega \) depends on the relative values of \( A_h \) and \( A_h \) and decreases with the decrease in ratio \( \frac{A_h}{A_h} \). In all the cases, the activation energy is underestimated. The present findings are in agreement with those reported by Sunta [19] for the case of linear heating scheme.

**4.0 CONCLUSIONS**

In the present paper, we have analysed saturated and unsaturated TL peaks recorded under hyperbolic or quadratic heating scheme in the framework of GOK, OTOR and IMTS models. In all the models, the peak temperature \( T_m \) depends on the Filling ratio \((f)\). For GOK model, the conventional peak shape method can be applied both for saturated and unsaturated TL peaks. For OTOR and IMTS models, peak shape method (\( \omega \)-formula) leads to appreciable errors in the calculation of activation energies of the saturated TL peaks. Even for the unsaturated TL peaks, the error increases with increasing e exc of retrapping. But the situation is not so grim because of two reasons. The first one is the experimental error in the determination of the activation energy. Keeping in mind the ranges of experimental error in the determination of \( E \), one can say that the peak shape method may be used at least for the preliminary estimation of \( E \). The second reason is that, there is still no experimental evidence of TL peaks with dominant retrapping. Considering these points one cannot completely rule out the applicability of peak shape method for the analysis of TL peaks recorded under hyperbolic heating scheme.
Table 3: Activation energies of some synthetic TL peaks by using ω-formula of peak shape method [16] calculated in the frameworks of IMTS model. Input parameters common to all the peaks are: $E = 1 \text{ eV}$, $s = 10^{12} \text{ sec}^{-1}$ and $N = 10^{12} \text{ cm}^{-3}$. Here $A[B]$ indicates $A \times 10^B$.

<table>
<thead>
<tr>
<th>$N$ ($\text{cm}^{-3}$)</th>
<th>$n_0$ ($\text{cm}^{-3}$)</th>
<th>$A_n$ ($\text{cm}^3\text{sec}^{-1}$)</th>
<th>$A_h$ ($\text{cm}^3\text{sec}^{-1}$)</th>
<th>Filling ratio (f)</th>
<th>$T_m$ (K)</th>
<th>$E_\omega$ (eV)</th>
<th>$\Delta E_\omega$ (%)</th>
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<td>1.0[12]</td>
<td>1.0[-7]</td>
<td>1.0[-10]</td>
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<td>384.5</td>
<td>0.817</td>
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<td>1.0[-2]</td>
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<td>0.858</td>
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<tr>
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<td>3.0[-3]</td>
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<td>2.0[-3]</td>
<td>388.5</td>
<td>0.855</td>
<td>14.5</td>
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<tr>
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<td>1.0[-4]</td>
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<td>383.8</td>
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<td>0.826</td>
<td>17.4</td>
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</table>

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