New handling of thermoluminescence glow curve deconvolution expressions for different kinetic orders based on OTOR model

Mohamed El-Kinawy, Hassan F El-Nashar* and Nabil El-Faramawy

Physics Department, Faculty of Science, Ain Shams University, 65511 Abbassia, cairo, Egypt.

*Corresponding author (for contact): e-mail: hbetterwork@gmail.com

Abstract. The exact equations of the thermoluminescence (TL) glow curve deconvolution that describe the intensity of a single TL glow peak of different order kinetics, which are obtained from the one trap-one recombination (OTOR) level model, are considered. The reformulation of the expressions of the intensities of TL glow peaks in terms of the peak intensity $I_M$, peak position $T_M$, and the activation energy $\epsilon$, for each order of kinetics are achieved. The authors developed a MATLAB computer code, which utilizes the obtained equations, to computationally deconvolute the TL glow curves. The code is used to investigate the reference glow curves of the GLOCANIN program. The obtained results agree with those previously reported by the GLOCANIN project with better values of the figure of merits FOM. The considerations of the obtained equations show promising trends to understand a peak formation for different order kinetics that belong to the OTOR level model.

1. Introduction

Thermoluminescence (TL) is the experimental observation of the stimulated emission of light upon heating up with a specific rate insulators and semiconductors that absorbed energy from radiation [1]. In order for the TL phenomenon to occur the material must possess impurities or defects, which play the role of trapping charge carriers migrating between the conduction and valence bands, with energy levels lie between the valence and conduction bands. The emitted light spectrum contains information about the energy levels of those defects of the TL material and its previous exposure to the ionizing radiations. Thus, to extract information from the emitted spectrum the recorded glow curve, the intensity of light as a function of temperature (or time), must be analyzed. In general, the TL glow curves look complicated where they do not have a simple mathematical formula capable of describing the intensity as a function of temperature. Theoretical models are proposed, in order to analyze the experimentally obtained TL glow curves, by considering these glow curves appearing convoluted of more than one glow peak. In this case, based on the suggested models, mathematical expressions are obtained to describe each individual TL glow peak and hence the resultant TL glow curve is composed of several individual peaks. Therefore, we are able to utilize the mathematical expressions by using the computational techniques to deconvolute the appeared TL glow curves into its individual constituents glow peaks.

Over the last few decades computerized glow-curve deconvolution (CGCD) has been considered to be the most common technique for the TL glow-curve analysis [2, 3]. The CGCD analysis is mainly used to find the individual glow-peak of a composite TL glow-curve and further to evaluate each glow-peak parameters [4, 5]. Based on several models, approximations and minimization procedures have been investigated and a number of computer programs have been developed for TL glow-curve analysis [6-
The computer programs employ different mathematical formulae, which express a single glow peak, are developed for the CGCD analysis. However, due to computational difficulties, the proposed mathematical expressions and CGCD programs use approximations. Currently, computational tools and software packages include many mathematical functions, which are built in. Therefore, they allow to evaluate mathematical expressions accurately.

The aim of the current study is going to consider the mathematical expressions that describe each individual glow peak, according to the one trap-one recombination (OTOR) level model. The exact equations of the TL glow peak are used and treated the mathematical terms that appear in the equations as exact functions without any approximations.

2. Models

In particular, according to the OTOR level model, there are three expressions for the intensity of each individual TL peak corresponding to three kinetic orders. For the first order kinetics, the intensity, for each peak, of the emitted light from the TL material following the first order kinetics is given by [11]

\[ I(T) = s n_0 \exp \left( -\frac{\epsilon}{kT} \right) \exp \left( -\frac{s}{\beta} \int_{T_0}^{T} \exp \left( -\frac{\epsilon}{kT'} \right) dT' \right) \]  

(1)

where, \( s \) is the frequency factor \((s^{-1})\), \( n_0 \) is the initial concentration of trapped electrons \( (cm^{-3}) \), \( \epsilon \) is the activation energy \( (ev) \), \( k \) is Boltzmann constant \( (J.K^{-1}) \), \( T \) is the absolute temperature \( (K) \), \( \beta \) is the heating rate and \( T_0 \) is the initial temperature of the heating profile. For the second and general order kinetics, the intensity of photons produced from the TL material is written as [12, 13]

\[ I(T) = S n_0^b \exp \left( -\frac{\epsilon}{kT} \right) \left[ 1 + S \frac{n_0^{b-1}(b-1)}{\beta} \int_{T_0}^{T} \exp \left( -\frac{\epsilon}{kT'} \right) dT' \right]^{\frac{1}{b-1}} \]  

(2)

where, \( S = s' \) for the second order kinetics model once \( b = 2 \) while in the general order model \( S = s'' \) and \( 1 < b < 2 \). It can be noticed that, from equations (1) and (2), that the number of charges, and hence the intensity of the glow peak, depends upon the integral \( \int_{T_0}^{T} \exp \left( -\frac{\epsilon}{kT'} \right) dT' \). Consequently, the solution of the integral can be as

\[ F_0(T, \epsilon, T_0) = \int_{T_0}^{T} \exp \left( -\frac{\epsilon}{kT'} \right) dT' \]  

(3)

This integral (3) is solved analytically [14-16] and it takes the following expression

\[ F_0(T, \epsilon, T_0) = T \exp \left( -\frac{\epsilon}{kT} \right) - T_0 \exp \left( -\frac{\epsilon}{kT_0} \right) + \frac{\epsilon}{k} \left( \text{Ei} \left( -\frac{\epsilon}{kT} \right) - \text{Ei} \left( -\frac{\epsilon}{kT_0} \right) \right) \]  

(4)

where \( \text{Ei}(x), x > 0 \), is the well-known exponential integral function [15]. Although, the previous integral has a solution, many works make approximations by taking few terms only of the solution of the previous integral [17-19], in order to obtain analytic expressions for describing the intensity as a function of \( T \) for a glow curve. The exponential integral function \( \text{Ei}(x) \) is a built in function in many symbolic calculation packages such as MATLAB and MATHEMATICA. Also, the integral (3) is solved analytically by the packages MATLAB and MATHEMATICA, where the same expression (4) is obtained. The previous packages are mentioned because anyone of them can be used in the computational analysis of the experimentally obtained TL glow curves. Thus, by considering the solution of the integral as in equation
(4), the exact equations of the OTOR level model in terms of the peak intensity $I_M$ and peak position $T_M$ can be reformed. A computer code using the MATLAB package is developed to study the de-convolution of several TL glow curves. The MATLAB package is used because it contains functions appearing in the solution of the integral as well as it includes excellent nonlinear curve fitting algorithms and suitable optimization methods for the TL glow-curve analysis. Moreover, our own code is developed to deconvolute the experimentally obtained TL glow curves because the commercial software's are not available and they always use approximations in regard to the solution of the integral (3). In addition, the high performance computers have limited precision and have only available accuracies of no more than 32 bits. Therefore, including many terms in the solutions of the integral (3) ensures a good level of accuracy in calculations and in general it allows overcoming the limitations of computer resources.

2.1. First order kinetics model

The intensity, according to equation (1), for the first order kinetics model can be written, using the solution of the integral (4), by inserting equation (4) into (1), as:

$$ I(T) = s_n \exp \left( \frac{\varepsilon}{kT} \right) \exp \left[ -s \left( T \exp \left( \frac{\varepsilon}{kT} \right) - T_0 \exp \left( \frac{\varepsilon}{kT_0} \right) + \varepsilon \left( \text{Ei} \left( \frac{\varepsilon}{kT} \right) - \text{Ei} \left( \frac{\varepsilon}{kT_0} \right) \right) \right] $$

Equation (5) gives the intensity of the TL peak according to the first order kinetic and it is a function of $s, \varepsilon, T, \beta$ and $T_0$. However, in computerized glow curve deconvolution (CGCD) analysis, it is desired to obtain a form of the intensity $I$, as a function of maximum TL intensity and its corresponding temperature (i.e. $I_M$ and $T_M$ respectively) [17], as well as the energy $\varepsilon$. In order to achieve the goal in accordance to the last sentence, the condition at maximum intensity is used and it is given by [17, 20]:

$$ s = \frac{\beta \varepsilon}{kT_M^*} \exp \left( \frac{\varepsilon}{kT_M^*} \right) $$

Inserting this condition (3) into equation (2) produces

$$ I_M = \frac{n_0 \beta e}{kT_M^*} \exp \left( -\frac{\varepsilon}{kT_M^*} \right) \exp \left( \frac{\varepsilon}{kT_M^*} F_0(T_M, \varepsilon, T_0) \right) $$

where $F_0(T_M, \varepsilon, T_0)$ is defined as

$$ F_0(T_M, \varepsilon, T_0) = T_M \exp \left( -\frac{\varepsilon}{kT_M} \right) - T_0 \exp \left( -\frac{\varepsilon}{kT_0} \right) + \varepsilon \left( \text{Ei} \left( -\frac{\varepsilon}{kT_M} \right) - \text{Ei} \left( -\frac{\varepsilon}{kT_0} \right) \right) $$

To obtain the intensity as a function of $I_M$, equation (7) is substituted into equation (5). Hence, an analytic expression for the intensity is found as:

$$ I = I_M \exp \left( \frac{\varepsilon}{kT_M} \frac{T - T_M^*}{T_M^*} \right) \exp \left( \frac{\varepsilon}{kT_M^*} \left( F_0(T_M, \varepsilon, T_0) - F_0(T, \varepsilon, T_0) \right) \right) $$

Equations (9), by the substitution from equations (3) and (8), is expressed as:

$$ I = I_M \exp \left( \frac{\varepsilon}{kT_M} \frac{T - T_M^*}{T_M^*} \right) \exp \left( \frac{\varepsilon}{kT_M^*} \left( F(T_M, \varepsilon) - F(T, \varepsilon) \right) \right) $$

where $F(T, \varepsilon)$ and $F(T_M, \varepsilon)$ are defined, respectively, as:
\( F(T, \epsilon) = T \exp \left( -\frac{\epsilon}{kT} + \frac{\epsilon}{k} \left( \text{Ei} \left( -\frac{\epsilon}{kT} \right) \right) \right) \)  \hspace{1cm} (11)

and

\( F(T_M, \epsilon) = T_M \exp \left( -\frac{\epsilon}{kT_M} + \frac{\epsilon}{k} \left( \text{Ei} \left( -\frac{\epsilon}{kT_M} \right) \right) \right) \)  \hspace{1cm} (12)

Equation (10) is now a function of \( I_{sh}, T_M, \epsilon, \) and \( T \), and it is ready to be used for a glow curve analysis. It is noticed that equation (10) is independent on the initial temperature of the heating process \( T_0 \).

2.2. Second-order kinetics

The second order kinetics is being as soon as \( b = 2 \) in equation (2). Therefore, the intensity of photons produced from the TL material is given by \[ I(T) = s'n_0^2 \exp \left( -\frac{\epsilon}{kT} \right) \left[ 1 + \frac{s}{\beta} \int_{T_0}^{T} \exp \left( -\frac{E}{kT'} \right) dT' \right]^2, \] \hspace{1cm} (13)

with \( n_0, \epsilon, T, \beta, \) and \( T_0 \) being the same parameters defined earlier. The quantity \( s' \) is the pre-exponential factor \( \left( \text{cm}^3 \text{ s}^{-1} \right) \). By substituting the solution of the integral (Eq. 3) into equation (13), the following expression for the intensity can be achieved

\[ I(T) = s' n_0 \exp \left( -\frac{\epsilon}{kT} \right) \left[ 1 + \frac{s}{\beta} F_0(T, \epsilon, T_0) \right]^2, \] \hspace{1cm} (14)

where \( s = s'n_0 \). In this case \( s \) has units \( s^{-1} \) similar to the frequency factor used in the first order kinetics but it is contingent upon \( n_0 \). In order to get a form of the intensity as a function of \( T_M, I_{sh}, T \) and \( \epsilon \), the condition at maximum intensity is used. In this case, of second order kinetics, it is given by [20]:

\[ S = \frac{\beta \epsilon}{2kT_M^2 \exp \left( -\frac{\epsilon}{kT_M} \right) - \epsilon F_0(T_M, \epsilon, T_0)} \] \hspace{1cm} (15)

Thus, the maximum intensity of the TL peak, following the second order model, is given by

\[ I_M = n_0 \frac{\beta \epsilon}{2kT_M^2 \exp \left( -\frac{\epsilon}{kT_M} \right) - \epsilon F_0(T_M, \epsilon, T_0)} \exp \left( -\frac{\epsilon}{kT_M} \right) \times \left[ 1 + \frac{\epsilon F_0(T_M, \epsilon, T_0)}{2kT_M^2 \exp \left( -\frac{\epsilon}{kT_M} \right) - \epsilon F_0(T_M, \epsilon, T_0)} \right]^2 \] \hspace{1cm} (16)

By substituting equation (16) into equation (14), the TL intensity \( I \) as a function of \( T_M, I_{sh}, T \) and \( \epsilon \) can be given by

\[ I(T) = I_M \exp \left( \frac{\epsilon}{kT} \left( \frac{T-M}{T_M} \right) \right) \left[ 1 + \frac{\epsilon F_0(T_M, \epsilon, T_0)}{2kT_M^2 \exp \left( -\frac{\epsilon}{kT_M} \right) - \epsilon F_0(T_M, \epsilon, T_0)} \right]^2 \] \hspace{1cm} (17)

Equation (17) can be simplified to take the form

\[ I(T) = I_M \exp \left( \frac{\epsilon}{kT} \left( \frac{T-M}{T_M} \right) \right) \left[ 1 + \frac{\epsilon F(T, \epsilon) - F(T_M, \epsilon)}{2kT_M^2 \exp \left( -\frac{\epsilon}{kT_M} \right)} \right]^2 \] \hspace{1cm} (18)

Equation (18) is the desired form which can be employed in the deconvolution analysis according to the second order kinetics and it is apparently independent of \( T_0 \). The two functions \( F(T, \epsilon) \) and \( F(T_M, \epsilon) \) are given by the two equations (11) and (12), respectively.

General order kinetics
Once the values of $b$ are $1 < b < 2$, a general order kinetics formula for the intensity of light emitted from the TL material, as suggested by May and Partridge [12], is obtained. In this case, this intensity is written as

$$I(T) = s'' n_0^b \exp \left( -\frac{\varepsilon}{kT} \right) \left[ 1 + \frac{s'' n_0^{b-1}(b-1)}{\beta} \int_{T_0}^{T} \exp \left( -\frac{\varepsilon}{kT'} \right) dT' \right]^{-\frac{b}{b-1}},$$  \hspace{1cm} (19)

where $s''$ is a pre exponential factor and it has the dimensions cm$^3(b^{-1})$ s$^{-1}$. Using the solution of the integral according to equation (3), equation (9) takes the form

$$I(T) = s n_0 \exp \left( -\frac{\varepsilon}{kT} \right) \left[ 1 + \frac{s(b-1)}{\beta} F_0(T, \varepsilon, T_0) \right]^{-\frac{b}{b-1}}.$$ \hspace{1cm} (20)

In equation (20) the frequency factor $s = s'' n_0^{b-1}$. In order to have a form of the intensity as a function of $T_M$ and $I_M$, the condition at maximum intensity is applied and it is given in this case by [19]:

$$s = \frac{\beta \varepsilon}{k b T_M^2 \exp \left( -\frac{\varepsilon}{kT_M} \right) [-\varepsilon(b-1)F_0(T_M, \varepsilon, T_0)]}.$$ \hspace{1cm} (21)

Inserting equation (21) into equation (20), at $T_M$, the maximum intensity $I_M$ is achieved, which is written as

$$I_M = \frac{n_0 \beta \varepsilon}{k b T_M^2 \exp \left( -\frac{\varepsilon}{kT_M} \right) [-\varepsilon(b-1)F_0(T_M, \varepsilon, T_0)]} \exp \left( -\frac{\varepsilon}{kT_M} \right) \left[ 1 + \frac{\varepsilon(b-1)F_0(T_M, \varepsilon, T_0)}{k b T_M^2 \exp \left( -\frac{\varepsilon}{kT_M} \right) [-\varepsilon(b-1)F_0(T_M, \varepsilon, T_0)]} \right]^{-\frac{b}{b-1}}.$$ \hspace{1cm} (22)

Thus, the TL intensity, as a function of $I_M$ and $T_M$ as well as $\varepsilon$ and $T$, is given by

$$I(T) = \frac{n_0 \beta \varepsilon}{k b T_M^2 \exp \left( -\frac{\varepsilon}{kT_M} \right) [-\varepsilon(b-1)F_0(T_M, \varepsilon, T_0)]} \exp \left( -\frac{\varepsilon}{kT} \right) \left[ 1 + \frac{\varepsilon(b-1)(F(T, \varepsilon) - F(T_M, \varepsilon))}{k T_M^2 b \exp \left( -\frac{\varepsilon}{kT_M} \right) [-\varepsilon(b-1)F_0(T_M, \varepsilon, T_0)]} \right]^{-\frac{b}{b-1}}.$$ \hspace{1cm} (23)

Equation (23) is simplified to take the form

$$I(T) = I_M \exp \left( \frac{\varepsilon}{kT} \left( \frac{T-T_M}{T_M} \right) \right) \times \left[ 1 + \frac{\varepsilon(b-1)(F(T, \varepsilon) - F(T_M, \varepsilon))}{k T_M^2 b \exp \left( -\frac{\varepsilon}{kT_M} \right) [-\varepsilon(b-1)F_0(T_M, \varepsilon, T_0)]} \right]^{-\frac{b}{b-1}}.$$ \hspace{1cm} (24)

Equation (24) is the required equation that can be used to achieve the TL glow curve analysis in view of the general order kinetics, where it shows the intensity as a function of $T$, $T_M$, $b$ and $\varepsilon$ and is independent on the initial temperature $T_0$. Equations (11) and (12), respectively, represent the two terms $F(T, \varepsilon)$ and $F(T_M, \varepsilon)$. 
A flow chart of the Matlab code

A flow chart describing the algorithm of the code is shown in figure 1. The first step is to enter the experimental data, temperature and intensity profiles $T$ and $I$. Next, the user chooses the desired equation to deconvolute the glow curve. The optimization method then begins by entering initial guess values of the optimization parameters ($\epsilon$, $T_M$, and $b$). The code provides the values of the optimization parameters. The user decides if the provided parameters are physically accepted. Otherwise the initial guess is altered until getting acceptable ones.

![Flow Chart of Matlab Code](attachment:flowchart.png)

Figure 1. The flow chart of the MATLAB code.

3. Deconvolution of GLOCANIN reference glow curves

Equation (10) is used to perform the CGCD analysis of the GLOCANIN reference glow curves of Bos et al. [21, 22]. The GLOCANIN glow curves include ten reference glow curves ensuing first order kinetics model only. The performance of fitting is tested with the figure of merit (FOM) as defined in reference [23]. Figures 2 and 3 show the CGCD analysis of the synthetic reference glow curves 1 and 2, respectively, according to the use of equation (10). The upper graphs of figures 2 and 3 indicate clearly the matching between the data points and the fitted curves. The lower patterns in both figures 2 and 3 demonstrate the residue (the difference between the data of the GLOCANIN curves and the fitted curve according to equation (10)). Figure 4 shows, in the upper graph, the de-convolution of the measured reference glow curve 9 using expression (10). In the lower plot of figure 4, the corresponding residue is presented. Table 1 presents a comparison between the FOM (%) values obtained by using our CGCD program, which employs the current TL expressions, a candidate in the intercomparison program of [20, 21], the Glow Fit program [24], and those of Kitis [17]. In table 2, the current results of the activation energies of the GLOCANIN ten glow curves, their corresponding Ref Glow in references [21, 22] and the average values of the activation energies in [17] are listed.
Figure 2. The deconvolution of the RefGlow.001 glow-curve of the GLOCANIN project [21, 22]).

Figure 3. The de-convolution of the RefGlow.002 glow-curve of the GLOCANIN project [21, 22]).

The GLOCANIN project [21, 22] includes only peaks subsequent to the first order kinetics model. However, there are no standard results or projects to test the second and the general order equations. A synthetic second and general order glow curves is generated by convoluting peaks using equations (13 and 19). Then, the resultant convoluted glow curves are deconvoluted again using the current recommended equations (18) and (24). The FOM values obtained in the case of the current proposed functions are of the order of 10-05 %, which is a very low value. The reason behind the low value comes due to including many terms, when the integral is considered in equations (13) and (19) to generate the synthetic glow curves for the second and general order kinetics as well as the use of equations (18) and (24). This indicates that the current expressions, for the intensities of the TL glow peaks as functions of T, give excellent results when they are used in the CGCD analysis.
Figure 4. The de-convolution of the RefGlow.009 glow-curve of the GLOCANIN project [21, 22].

Table 1. Comparison of the FOM [%] values obtained in the current work with those FOM values obtained in [21, 22], Glow Fit program [24] and those of Kitis [17].

| TL Data     | Glow Fit [24] FOM (%) | GLOCANIN Program B (Bos et al [21, 22]) FOM (%) | Kitis [17] FOM (%) | Current work FOM (%) |
|-------------|------------------------|------------------------------------------------|--------------------|---------------------|
| RefGlow.001 | 0.010                  | 0.010                                          | 0.006              | 0.0099              |
| RefGlow.002 | 0.010                  | 0.010                                          | 0.010              | 0.0099              |
| RefGlow.003 | 1.180                  | 1.150                                          | 1.040              | 0.9541              |
| RefGlow.004 | 1.060                  | 1.100                                          | 1.060              | 0.9815              |
| RefGlow.005 | 1.040                  | 1.070                                          | 1.050              | 0.6793              |
| RefGlow.006 | 1.230                  | 1.270                                          | 1.420              | 0.8723              |
| RefGlow.007 | 1.000                  | 0.950                                          | 0.910              | 1.0348              |
| RefGlow.008 | 0.920                  | 1.130                                          | 0.790              | 0.9048              |
| RefGlow.009 | 1.35                   | 1.700                                          | 1.060              | 0.8453              |
| RefGlow.010 | 3.860                  | 4.120                                          | 3.420              | 1.2874              |
Table 2. Results of the measured activation energies of the reference glow curves in comparison to those reported in references [17, 21-22].

| RGC       | Source                        | Peak 2 E (ev) | Peak 3 E (ev) | Peak 4 E (ev) | Peak 5 E (ev) |
|-----------|-------------------------------|---------------|---------------|---------------|---------------|
| RefGlow.001 | Current work                  | 1.183         |               |               |               |
|           | Kitis [17]                    | 1.182         |               |               |               |
|           | Used value [21]               | 1.182         |               |               |               |
| RefGlow.002 | Current work                  | 1.384         | 1.484         | 1.584         | 2.004         |
|           | Kitis [17]                    | 1.383         | 1.483         | 1.584         | 2.002         |
|           | Used values [21]              | 1.383         | 1.483         | 1.583         | 2.004         |
| RefGlow.003 | Current work                  | 1.224         | 1.311         | 1.604         | 2.136         |
|           | Kitis [17]                    | 1.230         | 1.314         | 1.582         | 2.190         |
|           | Avg value of Bos et.al [22]   | 1.260         | 1.330         | 1.620         | 2.1206        |
|           | Current work                  | 1.206         | 1.319         | 1.593         | 2.030         |
| RefGlow.004 | Current work                  | 1.227         | 1.321         | 1.564         | 2.102         |
|           | Kitis [17]                    | 1.224         | 1.330         | 1.630         | 2.080         |
|           | Avg value of Bos et.al [22]   | 1.468         | 1.544         | 1.483         | 2.173         |
|           | Current work                  | 1.206         | 1.319         | 1.593         | 2.030         |
| RefGlow.005 | Current work                  | 1.510         | 1.521         | 1.499         | 2.139         |
|           | Kitis [17]                    | 1.480         | 1.540         | 1.540         | 2.150         |
|           | Avg value of Bos et.al [22]   | 1.446         | 1.492         | 1.477         | 2.142         |
|           | Current work                  | 1.506         | 1.450         | 1.536         | 2.076         |
| RefGlow.006 | Current work                  | 1.480         | 1.510         | 1.510         | 2.170         |
|           | Kitis [17]                    | 1.480         | 1.510         | 1.510         | 2.170         |
|           | Avg value of Bos et.al [22]   | 1.990         |               | 2.170         | 1.990         |
|           | Current work                  | _             | 2.024         | 2.123         | 2.044         |
| RefGlow.007 | Current work                  | _             | 2.090         | 2.120         | 2.090         |
|           | Kitis [17]                    | _             | 2.090         | 2.120         | 2.090         |
|           | Avg value of Bos et.al [22]   | _             | 2.018         | 2.136         | 2.055         |
|           | Current work                  | _             | 2.018         | 2.136         | 2.055         |
| RefGlow.008 | Current work                  | _             | 2.090         | 2.120         | 2.090         |
|           | Kitis [17]                    | _             | 2.090         | 2.120         | 2.090         |
|           | Avg value of Bos et.al [22]   | _             | 2.018         | 2.136         | 2.055         |
|           | Current work                  | _             | 2.018         | 2.136         | 2.055         |
| RefGlow.009 | Current work                  | 1.221         | 1.305         | 1.555         | 2.062         |
|           | Kitis [17]                    | 1.257         | 1.305         | 1.591         | 2.026         |
|           | Avg value of Bos et.al [22]   | 1.250         | 1.300         | 1.600         | 2.020         |
|           | Current work                  | 1.235         | 1.557         | 1.498         | 2.066         |
| RefGlow.010 | Current work                  | 1.203         | 1.428         | 1.438         | 2.183         |
4. Formation of a peak

In order to understand the formation of each individual glow-peak and the terms control this formation, equations (10), (18) and (24) on the normalized form are rewritten as:

\[
\frac{I}{I_M} = \exp\left(\frac{\varepsilon}{kT} \frac{T-T_M}{T_M}\right) \exp\left(\frac{\varepsilon (F(T_M,\varepsilon) - F(T,\varepsilon))}{kT_M^2 \exp\left(\frac{-\varepsilon}{kT_M}\right)}\right) = f_1 f_2, \tag{25}
\]

\[
\frac{I}{I_M} = \exp\left(\frac{\varepsilon (T-T_M)}{kT_M}\right) \times \left[1 + \frac{\varepsilon (b-1)(F(T,\varepsilon) - F(T_M,\varepsilon))}{kT_M^2 b \exp\left(-\frac{\varepsilon}{kT_M}\right)}\right]^{-\frac{b}{b-1}} = f_1 f_i. \tag{26}
\]

When \( b = 2 \) is considered in equation (26), the model becomes the second order kinetics while for \( 1 < b < 2 \), the model converts to the general order kinetic one. According to equations (25) and (26) the first term, which is an exponentially growing term as a function of temperature, is common for the three models is given by:

\[
f_1 = \exp\left(\frac{\varepsilon (T-T_M)}{kT_M}\right). \tag{27}
\]

The second term, according to equation (25), controls the first order kinetics glow-peak shape, is written as

\[
f_2 = \exp\left(\frac{\varepsilon (F(T_M,\varepsilon) - F(T,\varepsilon))}{kT_M^2 \exp\left(\frac{-\varepsilon}{kT_M}\right)}\right). \tag{28}
\]

The first order kinetics peak finally comes out as \( f_3 = f_1 f_2 \times f_2 \). Figure 5 shows a plot of \( f_1, f_2 \) and \( f_3 \) as functions of \( T \). It is clearly indicated from figure 5 that the resultant peak appears as a contribution of an exponentially growing term \( f_1 \) and an inverted sigmoid term \( f_2 \).
Figure 5. The contribution of the two terms, $f_1$ and $f_2$, to form a first order glow-peak resultant normalized peak obtained by $f_1 \times f_2$.

For the second order kinetics model, the inverted sigmoid term $f_i = f_4$, when $b = 2$, is

$$f_4 = \left[ 1 + \frac{\epsilon (F(T, \epsilon) - F(T_M, \epsilon))}{kT_M^2 b \exp\left(\frac{-\epsilon}{kT_M}\right)} \right]^{-2}. \quad (29)$$

Finally, the inverted sigmoid term for the general order kinetics model ($1 < b < 2$), $f_i = f_6$, is:

$$f_6 = \left[ 1 + \frac{\epsilon (b-1)(F(T, \epsilon) - F(T_M, \epsilon))}{kT_M^2 b \exp\left(\frac{-\epsilon}{kT_M}\right)} \right]^{-\frac{1}{b-1}}. \quad (30)$$

The formation of the peak in accordance to the second order kinetics is shown in figure 6, which shows a plot of the terms $f_1, f_2$ and $f_3 = f_1 \times f_2$ as functions of $T$. In the case of the general order kinetics ($1 < b < 2$), figure 7 shows plots of $f_1, f_6$ and $f_7 = f_1 \times f_6$ as functions of $T$. 
Figure 6. The involvement of the two terms, $f_1$ and $f_4$, to shape a second order glow-peak. The resultant normalized peak obtained by $f_1 \times f_4$.

Figure 7. The role of the two terms, $f_1$ and $f_6$, on producing a general order ($b = 1.5$) glow-peak, which is a normalized peak once $f_1$ is multiplied by $f_6$.

Figures 5, 6 and 7 clearly indicate that the shape of each peak, in corresponding to each model, is controlled by a growth term and an inverted sigmoid term. Both terms, growth and inverted sigmoid, cross at $T_M$. The growth term depends on $T$, $T_M$, and $\epsilon$ and it is independent on the type of order kinetics. The inverted sigmoid term depends on the nature of order kinetics as well as $T$, $T_M$, and $\epsilon$. The effect of the inverted sigmoid term, when start, reduces the growing term as $T$ increases. However, the decay of the inverted sigmoid term as $T$ increases is different for each model. Thus, the resultant peak, according to the category of order kinetics, appear different due to different contribution of the inverted sigmoid terms, $f_2$, $f_4$ and $f_6$, for first, second and general order kinetics, respectively.
5. Conclusions
Within the frame of the OTOR level model, the exact equations of the intensities of a TL glow peaks as functions of temperature for different kinetics orders are preserved. The solution of the integral \( \int_{T_0}^{T} e^{\frac{-\epsilon}{kT}} dT' \), that appear in the model is considered. The exact equations of the OTOR level model in terms of the \( IM \) and \( TM \) to be used in the CGCD analysis are reformulated. The equations of different kinetic orders become \( T_0 \) independent as confirmed by experiments and approximations in previous works, although the solution of integral \( \int_{T_0}^{T} e^{\frac{-\epsilon}{kT}} dT' \) shows \( T_0 \) dependence. A computer code using the MATLAB package is developed to computationally deconvolute the TL glow curves. The CGCD analysis, using the equations of the first order kinetics, of the GLOCANIN reference glow-curves of references [14, 18-19] shows the capability of the current TL expressions to accurately analyze the TL glow-curves with very low values of FOM. The equations for the second and general order kinetics for the pre-constructed glow curves (synthetics) are tested and the obtained results of the computer program revealed excellent agreements with very low FOM values.

In the current study, the reformulation of the exact equations of the intensities as functions of \( T \) shows that the normalized TL glow peak for each model takes its shape in accordance to a contribution of two main terms. The first term contributes in a TL peak is a growth term, which is independent on the type of order kinetics. The second term is an inverted sigmoid dependent on the kind of the order kinetics. When the inverted sigmoid term starts to be effective, it compensates the exponential grow of the growth term and finally the peak takes its shape. In regard to the findings here, a further and a detailed study of equations (25)-(30), for several ranges of activation energies and temperatures, are required in order to understand the formation of a peak according to each model. The detail study may help to understand the factors that are responsible for the geometry of each peak in accordance to each form of order kinetics.

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