Glow Curve Analysis and Calculation of Thermoluminescence Parameters

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Abstract: A new method for analysis of the glow curve with one maximum is described. This method is based on fitting the experimental glow curve with a new type of asymmetric Gauss-Lorentz (GL) function. This function was adapted to be very precise in describing glow curves. A completely new algorithm for calculating the kinetic parameters of the process for the OTOR (One Trap-One Recombination center) model or the model of ideal phosphor was developed. The kinetics order concept was used for calculation of the kinetic parameters of the process. The kinetics order parameter was defined by means of real physical parameters. A new function was proposed to describe the dependence of the factor symmetry of order kinetics. It has enabled a very accurate calculation of the activation energy parameter. The resulting relative error was less than 0.5%.

Keywords: Thermoluminescence, Kinetics order, Glow curve, Kinetics model, Activation energy

1 Introduction

For an accurate and reliable thermoluminescent analysis, it is important to know the physical models describing TL relaxation [1,2]. In this case, it is possible to connect them with practical experiments and carry out the procedure for their qualitative and quantitative evaluation. The experimental glow curve, with the use of certified and valuable physical models can provide accurate calculation of the physical parameters of the TL process [3,4,5,6,7,8,9,10]. If the accuracy of the obtained parameter values is confirmed by other methods of analysis and measurement, this is a reliable indicator that a given model can be used. The calculated values of the kinetic parameters of the real model can be used for reconstruction of the TL process, its analysis, and for its better understanding.

The general order kinetics model is commonly used for TL analysis [5,11–14]. It is a mathematical model, which is designed to describe the shapes of glow curves. Therefore,
the use of this model for calculating the real physical parameters is limited or excluded. It can be shown in many cases, in practice, that some physical parameters can not be calculated, and the calculated values of other parameters are not accurate enough. The use of realistic physical models, due to difficulties with the calculation of the process parameters, has almost completely been eliminated. This significantly limits the understanding of the process and slows down progress in understanding complex phenomena. An important step in further progress in the research of the existing model is to develop an algorithm for the calculation of real physical parameters.

A number of different models exist in the theory of TL processes [1–3, 6, 7, 14, 16–19]. One of the important tasks is a good estimate which of the existing models is applicable. This ensures that the values of the kinetic parameters of the TL process are accurately calculated. Another important task is to develop an algorithm for accurately calculating the parameters. This means that for each model there is a corresponding calculation algorithm. Specific tasks, dealing with the development of the calculation algorithms are: determination of model restrictions, which parameters have the greatest influence on the process, which parameters can be independently calculated, and so on. Answers to these questions enables improvement of existing models and development of new advanced models.

The main objective of this paper is calculation of the real physical parameters of the glow curve based on an experimentally obtained TL curve followed by reconstruction of the physical process of TL relaxation. Therefore, criteria enabling estimation of the model describing the kinetics of the process must be developed first. Practice has shown that visual evaluation of the kinetics model is not possible as it requires more accurate and reliable criterion. It is very important to accurately calculate the parameters of the process [20].

In this paper, calculation of the physical parameters of the process was applied only to the model of ideal phosphor. This model is based on theoretical differential equations that describe the kinetics of the process in ideal phosphors and are given in the following books and papers [3, 17, 21, 22]. The term ideal phosphor involves phosphors that can be modeled with one type of traps and one type of light emission center.

The algorithm for calculation of the parameters of TL kinetics, for the model of ideal phosphors, was based on the concept of kinetics order [1, 2, 12–14]. In order to apply this concept it is necessary to define kinetics order in a new way. Definition of kinetics order applied in the general order kinetics is completely inappropriate for the model of ideal phosphors. The equation for calculating the activation energy is used to define a kinetics order parameter.

Starting from this equation glow curves were analyzed for typical values of kinetic parameters. Based on these results, the relationship between the order of kinetics \( l \) and symmetry factor \( \mu_s \) was determined. This relationship enabled the use of the main principles of an existing algorithm, from the general order kinetics model, to calculate the activation energy \( E \) [5, 7, 13, 20].
2 Asymmetrical Gauss Lorentz function

It has previously been shown that the TL relaxation rate or phosphorescent decay follows an exponential law in the case of first-order kinetics and an approximately hyperbolic law in the case of second-order kinetics.

From there, with respect to the linear heating rate, one can assume that the first order kinetics curve can be approximated with the Gauss function and the second order kinetics can be approximated with the modified Gaussian or GL function [20, 24].

In general, it can be assumed that the glow curve, whose kinetic order value is between one and two, can be described with a curve that connects the Gauss and Lorentz functions. One form of the function, connecting the Gaussian and Lorentz curves, is given as:

\[
I = I_m \left\{ 1 + \left( 2^Z - 1 \right) \frac{\exp \left( \frac{\ln(1+b) - \ln(1-b)}{|\ln(1+b) - \ln(1-b)| (T-T_m)} \right) - 1}{b^2} \right\}^{-\frac{1}{2}}
\]

where \( I_m \) is the maximum value of the function, \( T_m \) is the position of the maximum, \( \omega \) is the half-width, \( b \) characterizes the degree of asymmetry, and \( Z \) is a parameter determining the shape. For \( Z=1 \) eq. (1) describes the Lorentz function and for \( Z \to 0 \) the Gauss function. For \( Z<1/12 \) eq. (1) differs negligibly from the Gauss function [20].

It can be shown that equation (1) can be successfully used for fitting synthetic glow curves and real glow curves with one maximum. Complex analysis of a real glow curve assumes its comparison with theoretical curves.

3 Evaluation the applicability of models

Experimental glow curves with one maximum are the consequence of the fact that phosphor contains only one type of active traps. The simplest physically realistic process, which is described by the glow curve with one maximum, occurs in the case of phosphor consisting of one type of traps and one type of luminescent centers. This model is known as the OTOR model (One Trap-One Recombination center) or the model of ideal phosphor [2, 17]. A more complex model, consisting of one type of active traps, one type of isolated or inactive traps and one type of recombination centers, is called the non-interactive kinetics model or the NMTS model (Non-interactive MultiTrap System) [1, 2]. The model of ideal phosphor determines the limit of applicability of the NMTS model, as it is applied in the case of a negligible concentration of inactive traps. The kinetics model, which is known as the model of mixed order or the MO model (Mixed Order) [2, 15, 17, 23], is only one special form of non-interactive kinetics.
A general differential equation that describes the kinetics of these models is given as [1,2]:

\[ I = -\frac{dp_l}{dt} = \frac{s \exp\left(-\frac{E}{kT}\right) n(n+m)}{(n+m)+r(N-n)} \]  

(2)

where at a time \( t \) (s), \( I \) (cm\(^{-3}\)s\(^{-1}\)) is the TL intensity, \( p_l \) (cm\(^{-3}\)) is the concentration of luminescent centers, \( n \) (cm\(^{-3}\)) is the electron trap concentration, \( N \) (cm\(^{-3}\)) is the concentration of active traps, \( m \) (cm\(^{-3}\)) is the initial electron inactive trap concentration, \( s(s^{-1}) \) is the frequency factor, \( E \) (eV) is the energy depth of a single active trap, \( T \) (K) is the material temperature, and \( k \) (eVK\(^{-1}\)) is the Boltzmann constant, \( r \) is \( \gamma_f/\gamma_i \), where \( \gamma_f \) (cm\(^3\)s\(^{-1}\)) and \( \gamma_i \) (cm\(^3\)s\(^{-1}\)) are the recombination probabilities between the conduction band electrons and the traps or the luminescent centers, respectively. To obtain this equation, an approximation describing the quasi-stationary equilibrium of electrons in the conduction band is used. This approximation assumes that the rate of change of the concentration of electrons in the conduction zone is much smaller than the speed of change of the electron in the traps. Inactive traps are, in fact, deep traps, which cannot be filled and emptied during thermal relaxation. Equation (2) describes the NMTS model, for \( r=1 \) it describes the MO model, and for \( m=0 \) it describes the OTOR model or the model of ideal phosphor. Equation (2) can be written as follows:

\[ I = -\frac{dn}{dt} = \frac{s \exp\left(-\frac{E}{kT}\right) n}{1+r\frac{n}{N}m} = Sn \left(\frac{1+r\alpha}{1+r\alpha\left(\frac{1}{2}-1\right)}\right) \]  

(3)

where \( S = \exp(-E/kT) \), \( f = n/N \) is the filling factor, and \( \alpha = n/(n+m) \) is the factor that directly determines the value of kinetic order in the model of mixed-order kinetics. It can be concluded that factor \( \alpha \) determines the shape of the glow curve, in the same manner as the retrapping factor \( r \). The \( r\alpha/f_0 \) ratio determines whether the parameter kinetics order will have a value between one and two. The values of this ratio may be the same for a large number of different values of parameters \( r, a_0 \) and \( f_0 \), where \( f_0 = n_0/N, a_0 = n_0/(n_0+m) \) is the initial electron concentration in the active traps. Therefore, it is necessary to choose the value of the \( f_0 \) factor. This factor can have any value in the range from 0 to 1. For simplicity it can be assumed that \( f_0=1 \). Based on this it was possible, to make the diagram describing how the value of the shape factor \( \varepsilon \) depends on the symmetry factor \( \mu_s \), for glow curves obtained by numerical solution of differential equations (3), for defined parameter values \( s, E, r, f_0, a_0 \) (Fig.1.) [25]. Parameters \( s \) and \( E \) determine the position of the diagram in Fig.1., using the values of parameter \( \Delta = 2kT_m/E \), where \( T_m \) is the temperature of the glow curve maximum. When the value of parameter \( \Delta \) decreases, the position of the curves in the diagram are shifted to the left (curve 3 in the diagram), and in the opposite case to the right.

Good evaluation of the model, where TL relaxation takes place, requires calculation of the value of \( \Delta \), for a glow curve that is experimentally obtained. This value, with sufficient
Glow Curve Analysis and Calculation of Thermoluminesce Parameters

Fig. 1. Criteria for determining which kinetic model can describe a certain glow curve, for the value of $\Delta = 0.07957$, for different values of parameters $r$ and $\alpha$: 1-model of ideal phosphor $\alpha = 1$, $\alpha_1 = 0.3$, $\alpha_2 = 0.5$, $\alpha_3 = 0.7$, $\alpha_4 = 0.8$, $\alpha_5 = 0.85$, $\alpha_6 = 0.9$, $\alpha_7 = 0.96$, 2-mixed order kinetics model $r=1$, $r_1=0.1$, $r_2=0.3$, $r_3=0.7$, $r_4=1.5$. The criteria, for the model of ideal phosphor, for the value of $\Delta = 0.037545$ is shown with a dot-dash line (3). Values, which were determined for some dosimeters, are shown as follows: P1(#) - TLD700H(\(^7\)LiF:Mg,Cu,P), P2(+) - TLD400(CaF:Mn) i P3(x) - TLD500(Al\(_2\)O\(_3\):C).

Accuracy, can be determined relatively easily using existing iterative methods. Such an iterative method is described in this paper. The procedure used in the calculation of the model parameters in general-order kinetics can also be used.

Analysis of a large number of theoretical curves for the NMTS model, enabled conclusion that the factors describing the shape ($Z$) and asymmetry ($b$) of the curves, change in different ways, depending on the values of the parameters that define the kinetics of the process. This allows determination whether the kinetic process can be described using a model of an ideal phosphor or mixed-order kinetics model or models of noninteractive kinetics using a simple determination of their values.

Values of the shape factor and symmetry factor were determined and are shown in Fig.1 for some typical TL dosimeters [10, 16, 26–29].

4 Advanced asymmetric Gauss-Lorentz function

In the analysis of TL glow curves with GL functions, it has been noted that in some cases they cannot be described with sufficient precision. It is shown that values of the shape and the asymmetry factor, for any particular TL glow curve are not constant [2, 14, 22]. Thus,
at the beginning of the glow curve, TL relaxation may be followed by first order kinetics, while the second order kinetics can be applied at its end. The opposite may apply too. In both cases the factor asymmetry and the shape factor have different values at the start and at the end of the process. In areas where the change in the value of factors is significant or where the changes oscillate, imprecision in describing the curves is higher.

Function (1) has five parameters, and if the normalized curve is used, which is applicable to curves with only one peak then it has four parameters. The geometrical parameters \( \omega \) and \( T_m \) can be taken from the glow curve directly and they are important characteristics. Precise calculation of these parameters is especially important for calculating values of physical parameters of the kinetic process. Therefore, it was assumed that their value depended on the time at which the process was observed. Then it can be assumed that the factors of asymmetry and shape factors have changeable values versus time \( t \), or versus heating temperatures \( T \). Analysis of synthetic TL glow curves showed less accurate fitting with the GL function, in areas where significant changes in the shape factor occurred. It can be concluded that the shape factor is a more complex function than the asymmetry factor. Therefore, it is appropriate that the shape factor \( Z \) is approximated by the following function:

\[
Z = z_2 (T - T_m)^2 + z_1 (T - T_m) + z, \tag{4}
\]

and the factor of asymmetry with a linear function:

\[
b = b_1 (T - T_m) + b_0 \tag{5}
\]

After replacing the expressions for the shape factor (4) and the symmetry factor (5) in equation (1), the new, improved GL function is obtained. This function has three new parameters and computer simulated curves showed better fitting of the TL glow curves.

5 Kinetics of the model of ideal phosphors

After substitution of \( \alpha = 1 \) in (3), the equation of the model of ideal phosphors is obtained:

\[
I = -\frac{dn}{dt} = n s \exp \left( -\frac{E}{kT} \right) \frac{S_n}{1 + r \left( \frac{n}{N} - 1 \right)} \tag{6}
\]

When \( r=0 \) then equation (6) becomes the equation of first order kinetics models, and when \( n<<N \) or \( r=1 \) it becomes the equation of the second order kinetics model. At the beginning of the TL relaxation time \( t=0 \), the expression in the denominator of equation (6) will be:

\[
1 - r + \frac{r}{f_0} \tag{7}
\]

where \( f_0 = n_0/N \) is the filling factor of traps at time \( t=0 \). The filling factor has a value from 0 to 1. It may be noted, that when the value of \( r \) is greater than one then the value of the
kinetics order is greater than two, due to high electron retrapping. When \( r < f_0 \), there are two cases. For \( r < f_0 \) TL relaxation kinetics follows the first-order kinetics model, due to very low retrapping. The kinetics, which can be defined as kinetics of the \( l \)-th order, corresponds to the case when \( r \approx f_0 \), and when the value of \( r \) is less than \( f_0 \) in less than two orders of magnitude. It should be noted, that even with very low occupancy of traps kinetics of the \( l \)-th order may occur, if the value of the retrapping factor is also proportionately very small.

In general, equation (6) cannot be solved, making it difficult to analyze the characteristics of the model and analysis of experimental curves. Therefore, the exponential type GL function and concept of kinetics order have been used, for analysis of the characteristics of TL kinetics. To make the concept of kinetics order could be used in realistic physical models, it is necessary previously defined parameter of kinetics order using real physical parameters.

6 Kinetics order concept

The concept of kinetics order is based on a model of general-order kinetics, which approximately describes the real experimental glow curves in the range between the first and second order kinetics [11–14]. Practice has shown that this is quite an inaccurate approximation, and does not enable calculation of all parameters. Values of the activation energy of traps can be calculated approximately, while other parameter values parameters cannot even be roughly estimated. However, the concept of order kinetics has demonstrated that a theoretical curve can be obtained, which is nearly a perfect match with experimental curves, and parameters of the theoretical curve are not derived from the process of TL relaxation. These parameters are the result of mathematical assumptions. Therefore, reconstruction of the kinetics of the TL process is not possible based on these values. This prevents successful research and understanding of the kinetics of TL relaxation. It has been shown, that one of the results of applying the concept of order kinetics is that the values of activation energy of traps can be calculated using the relation [5, 13]:

\[
E = \frac{lkT_m^2}{\delta_{eff}}
\]

where \( l \) is the kinetics order, \( \delta_{eff} \) is the part of the integral of glow curve from the maximum to its end. It should be noted that this solution is obtained by analytically solving a differential equation, which describes the general order kinetics model [5]. Since the glow curve of the general order model may perfectly fit any experimental TL curve, it can be concluded that equation (8) can also be applied to any experimental curve. This can be proved, because the same equation is used to calculate the activation energy for the cases of models of first order [3,18,30], second order [3,19,30] and mixed order [6,7,31].

When equation (8) is used, in order to calculate the values of experimental parameters
of the glow curve, the values which are obtained, sometimes, considerably deviate from accurate values. In equation (8) \( k \) is a constant, and parameters \( T_m \) and \( \delta_{\text{eff}} \) are geometrical parameters, which can be very accurately obtained from experimental curves. Obviously, deviation from the correct value is due to the inability to determine the exact value of the kinetics order \( l \). It was concluded, based on comparisons of differential equations of the model of ideal phosphor and general order kinetics model that this is due to changes in the value of parameter \( l \), for the duration of the relaxation process. Thus, parameter \( l \) is related to the kinetics of the process and cannot be calculated. However, there are no processes of the \( l \)-th order, but processes of the first and second order kinetics. The equation for calculating the activation energy, for the mixed-order kinetic model [7], indicates that parameter \( l \) has a constant value. It refers to a previously determined glow curve, and depends on initial conditions. This means that for the same phosphors different values of order kinetics may be obtained if the initial conditions are different. Therefore, the value of kinetics order, which is constant, can be calculated for each experimental curve. On the basis of this conclusion, it is possible to introduce an expression that defines the kinetics order for the model of ideal phosphor:

\[
l = \frac{E \delta_{\text{eff}}}{kT_m^2}
\]

The value of kinetics order, which is defined in such a way, should be introduced in the calculation algorithm, in order to obtain the correct values of physical parameters. In all the above models, the same principle is used to develop the calculation procedures. This ensures accurate calculation of the parameters of TL kinetics.

When the concept of kinetics order is applied to a model of ideal phosphor, it is necessary to examine the effect of the \( rf_0 \) ratio on the shape of the glow curve, or on the value of parameter \( l \). After testing a large number of glow curves, it was determined that the function \( rf_0 \) versus \( l \), depends only on the initial occupancy of traps \( f_0 \). Figure 2 shows this dependence, in the range of parameter values of practical interest for the analysis of experimental glow curves with one maximum. The obtained diagram is generally valid, for the model of ideal phosphors. Therefore, this diagram can be used to calculate the kinetic parameters of TL.

7 Calculating the parameters of the model of ideal phosphors

When the theoretical equation (6) is used for reconstruction of the kinetics of the TL process, it is necessary to know the values of the parameters that define the process. For the normalized glow curve it is necessary to know the values of parameters \( s, r, f_0 \) and \( E \).

The glow curve must be presented in an analytical form for quick and accurate analysis. Analysis of the glow curve, which uses the improved GL function of the exponential type,
allows accurate calculation of geometrical parameters $T_m$, $\delta_{eff}$ and $\mu_x$ [20,32]. Using equation (8) and the diagram in Fig.2 it is possible to determine the values of activation energy $E$ and the $r/f_0$ ratio. First, the value of kinetics order $l$ has to be calculated.

Kinetics order is determined from the diagram that describes how the symmetry factor $m_s$ is dependent on the kinetics order, for different values of $\Delta = 2kT_m/E$. The method is based on an iterative procedure and on the proven assumption that the value of $\Delta$ is located within a limited range of values, from 0.03 to 0.15. For this entire range, a functional dependence of $\mu_x(l)$ exists allowing calculation of the value of $l$.

If it is assumed that the $r/f_0$ ratio is in the range of 0 to 3, then glow curves obtained by numerical solution of the differential equation (6) can be analyzed for four groups of initial values. Differential equations were solved numerically using the Runge Kutta IV order. Four groups of parameter values were chosen to cover all values of $\Delta$, which are of interest (from 0.03 to 0.15): the first group $E_1=3eV$, $s_1=10^{22}s^{-1}(\Delta_1=0.03755)$, the second group $E_2=1eV$, $s_2=10^{12}s^{-1}(\Delta_2 = 0.06605)$, the third group $E_3=0.2eV$, $s_3=10^{8}s^{-1}(\Delta_3 = 0.09865)$ and the fourth group $E_4=0.1eV$, $s_4=10^{5}s^{-1}(\Delta_4 = 0.14815)$. The value of the filling factor of traps was taken to be $f_0=1$, to ensure that changes in $\Delta$ values are as little as possible, for glow curves of the same group. Obtained simulated curves were analyzed using the improved GL function of the exponential type. The value of $T_m$ can be obtained directly by fitting, while parameters values $\delta_{eff}$ and $\omega_{eff}$, required application of numerical calculation methods. Parameter $\omega_{eff}$ is the integral of the normalized glow curve. Then, the following values were calculated: $l$ from equation (9) and $\mu_x$ from the $\delta_{eff}/\omega_{eff}$ relationship. The resulting function $\mu_x(l)$ can be represented with the following empirical function with sufficient precision:

\[ \mu_x = \mu_{s0} + A_1 l^2 + A_2 \ln l \]  

(10)

Coefficients, $\mu_{s0}$, $A_1$ and $A_2$ are linear functions of $\Delta$. It enables quick and accurate calculation of the values of kinetics order. The results are shown in Table I and Fig.3.

<table>
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<th>$\Delta$</th>
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An iterative procedure must be established to calculate the value of kinetics order, using the diagram in Fig.3. First, a value of $\Delta$ is assumed (eg about 0.1). Then, the value of kinetics order $l$ is calculated, with the use of the corresponding curve in Fig. 3. The value
of the activation energy $E$ is calculated using equation (8). This value is substituted in the equation $2kT_m/E$ to calculate $\Delta$, and its new value is calculated. The resulting new value of $\Delta$ is more accurate than the previous one. The new value is used in the next step. This procedure may be repeated until the value of kinetics order reaches the desired accuracy. Usually, three or four iterations are necessary, in order to achieve satisfactory accuracy.

For a complete analysis and determination of all parameters necessary for the reconstruction of the glow curve, the value of the frequency factor must also be calculated. The value of the frequency factor, for the model of first order kinetics is calculated from the equation:

$$s = \frac{RE}{kT_m^2} \exp\left(\frac{E}{kT_m}\right)$$

where $R$(K/s) is the heating rate of phosphor. However, it has been proved that it is not possible to calculate values of the frequency factor for models of the second-order [33], mixed order [7] and general order [5, 13]. The derived theoretical equations enable calculation of only a pre-exponential factor, in which the frequency factor is one of the factors.

The frequency factor determines the probability of emission of electrons from electron traps, for high values of the heating temperature. Then the value of the exponential factor $\exp(-E/kT_m)$ is approximately equal to one. When, there is a high concentration of empty traps in the phosphor material and when the value of the retrapping factor is not negligible then a significant number of electrons are retrapped. This can be seen on the glow curve,

**Fig. 2.** The diagram shows how the ratio between the retrapping factor and filling factor depends on the kinetics order, for different filling factor values.
as the TL peak shifts to higher values as a result of reducing the velocity of luminescent recombination. Since the filling factor of traps is not known, it is not possible to make a correction of its influence on the rate of TL relaxation.

In the initial stage of relaxation, the relative impact of retrapping is very small, because the total amount of electrons, which are retrapped in phosphor, is small. This means that, in the initial phase, the glow curve does not depend on the retrapping factor and the filling factor. Therefore, the temperature of the maximum will be shifted towards lower temperature values, because significant redistribution of the electrons from the trap will be performed only after the maximum. In this case, the correction, that needs to be done, depends on the kinetics order \( l \) and factor \( \Delta \). For the range of kinetics order values between 1 and 2, the following expression is obtained [34]:

\[
s = \frac{R}{2 - l + \mu_s f_0 (l - 1)} \exp \left( \frac{E}{kT_m} \right)
\]  

(12)

For the value of \( f_0=1 \), in the phosphor material, there are no empty traps and then the above formula may be used to calculate values of the frequency factor. In other cases, the formula can be used to calculate the pre-exponential factor.

Models of the first and second order kinetics are special cases of the kinetics model of ideal phosphors. For the first-order kinetics model, after substitution of \( l=1 \), equation (12) becomes the same as equation (11). For the second-order kinetic model, after substitution
of \( l=2 \), the corrective factor of equation (12) becomes \( 1+0.9\Delta \). In the theory of this model, this factor should be \( 1+\Delta \). The difference between corrective factors is negligible, because, in both cases, they are obtained by approximation, and the values of \( \Delta \) are very small.

8 Results

The algorithm for calculating the kinetics parameters of TL, for the model of ideal phosphor, was tested on a number of computer-simulated glow curves. Values of parameters characterizing phosphors \( (r,E,s) \) and the parameter \( f_0 \), which determines the initial value of relaxation were selected for the model of ideal phosphors shown by differential equation (6). For simplicity of calculation, it was taken that in all cases the heating rate of phosphors is \( R=1\text{K/s} \). The parameter values were chosen so that the values of order kinetics were between 1 and 2, and corresponded to the values that characterize phosphors in dosimetry. These values, for some characteristic cases, are shown in Table II. The \( r/f_0 \) ratio is separately shown in the Table, due to its special relevance in the calculation of values of kinetics order. Simulated glow curves were obtained for the parameter values given in Table II, and using the numerical method of Runge Kutta IV order to solve differential equation (6). Glow curves were normalized, and then adjusted with improved GL functions of the exponential type. Results of fitting are shown in Table III.

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<td>0.9</td>
<td>0.9</td>
<td></td>
</tr>
</tbody>
</table>

In Table III, \( \chi^2 \) or chi-square is a quantity that determines the quality of fitting.

Displaying the glow curve in analytical form allows precise determination of parameters, which is especially important for the \( T_m \) value, since it is in an exponential function. Also, the value \( \delta_{eff} \) was calculated more easily and more accurately. This value is very difficult to calculate precisely, because glow curves asymptotically approach the zero value at the end of the relaxation process. Parameter values \( \delta_{eff}, \omega_{eff} \) and \( \mu_e \) were numerically
Glow Curve Analysis and Calculation of Thermoluminescence Parameters

Table III. Results of fitting glow curves, from Table II., with the GL function

<table>
<thead>
<tr>
<th>No</th>
<th>$T_m$</th>
<th>$\omega$</th>
<th>$\phi_1$</th>
<th>$\phi_2$</th>
<th>$h_0$</th>
<th>$h_1$</th>
<th>$\chi^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>466.67</td>
<td>19.00</td>
<td>0.0558</td>
<td>0.00923</td>
<td>-0.2855</td>
<td>3.34x10^{-4}</td>
<td>2.22x10^{-6}</td>
</tr>
<tr>
<td>2</td>
<td>147.55</td>
<td>11.32</td>
<td>0.1130</td>
<td>0.01368</td>
<td>1.58x10^{-4}</td>
<td>-0.2408</td>
<td>4.11x10^{-4}</td>
</tr>
<tr>
<td>3</td>
<td>721.79</td>
<td>69.38</td>
<td>0.0093</td>
<td>0.00232</td>
<td>6.17x10^{-6}</td>
<td>-0.2729</td>
<td>8.70x10^{-4}</td>
</tr>
<tr>
<td>4</td>
<td>53.653</td>
<td>5.657</td>
<td>-0.0543</td>
<td>0.02887</td>
<td>1.16x10^{-6}</td>
<td>-0.2901</td>
<td>0.01181</td>
</tr>
<tr>
<td>5</td>
<td>1174.0</td>
<td>168.8</td>
<td>0.0086</td>
<td>3.66x10^{-4}</td>
<td>7.77x10^{-7}</td>
<td>-0.2808</td>
<td>1.44x10^{-4}</td>
</tr>
<tr>
<td>6</td>
<td>317.76</td>
<td>49.06</td>
<td>0.0317</td>
<td>3.10x10^{-3}</td>
<td>1.26x10^{-5}</td>
<td>-0.2395</td>
<td>8.85x10^{-4}</td>
</tr>
<tr>
<td>7</td>
<td>73.64</td>
<td>87.74</td>
<td>0.3906</td>
<td>9.73x10^{-4}</td>
<td>-1.62x10^{-6}</td>
<td>-0.0303</td>
<td>3.37x10^{-4}</td>
</tr>
<tr>
<td>8</td>
<td>322.68</td>
<td>65.00</td>
<td>0.4236</td>
<td>1.42x10^{-3}</td>
<td>-2.68x10^{-6}</td>
<td>0.0598</td>
<td>-1.01x10^{-3}</td>
</tr>
<tr>
<td>9</td>
<td>53.382</td>
<td>7.166</td>
<td>0.4031</td>
<td>0.01068</td>
<td>-2.70x10^{-6}</td>
<td>0.0069</td>
<td>-5.47x10^{-4}</td>
</tr>
<tr>
<td>10</td>
<td>1166.7</td>
<td>228.3</td>
<td>0.3445</td>
<td>2.16x10^{-4}</td>
<td>-3.23x10^{-6}</td>
<td>0.1088</td>
<td>-1.30x10^{-4}</td>
</tr>
</tbody>
</table>

Calculated and are shown in Table IV. Romberg’s method was used for the calculation of $\delta_{eff}$ and $\omega_{eff}$ integrals.

Based on the parameter values of $\delta_{eff}$, $\mu_s$ and $T_m$ given in Tables III and IV, and using the previously described procedure for calculation, it is possible to calculate values of parameters of glow curves $E$, $l$, $r$, $\Delta$ and $s$. Table V shows the calculated values of these parameters $E_{c}$, $l_{c}$, $r_{c}$, $\Delta_{c}$ and $s^{(0)}$. The relative errors of calculation of parameters $E$ and $r$ can be determined, since their exact values are known. For parameter $s$, it is possible only when $f_0=1$, as then values of the pre-exponential and frequency factor are identical. The exact values of parameters $l$ and $\Delta$ are not known, so it is not possible to calculate their relative errors. The accuracy, with which it is possible to calculate individual parameters can be estimated by analyzing values of the relative error. This analysis also provides an assessment of the validity of the method used for the calculation of parameters [34].

Table IV. Calculated values of glow curve parameters

<table>
<thead>
<tr>
<th>No</th>
<th>$\omega_{eff}$</th>
<th>$\delta_{eff}$</th>
<th>$\mu_s$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>21.911</td>
<td>9.1504</td>
<td>0.41762</td>
</tr>
<tr>
<td>2</td>
<td>12.940</td>
<td>5.5918</td>
<td>0.43213</td>
</tr>
<tr>
<td>3</td>
<td>78.701</td>
<td>33.135</td>
<td>0.42102</td>
</tr>
<tr>
<td>4</td>
<td>6.3718</td>
<td>2.6382</td>
<td>0.41404</td>
</tr>
<tr>
<td>5</td>
<td>182.63</td>
<td>75.432</td>
<td>0.41304</td>
</tr>
<tr>
<td>6</td>
<td>54.967</td>
<td>24.011</td>
<td>0.43683</td>
</tr>
<tr>
<td>7</td>
<td>99.790</td>
<td>50.150</td>
<td>0.50255</td>
</tr>
<tr>
<td>8</td>
<td>73.288</td>
<td>39.206</td>
<td>0.53495</td>
</tr>
<tr>
<td>9</td>
<td>8.1341</td>
<td>4.1886</td>
<td>0.51494</td>
</tr>
<tr>
<td>10</td>
<td>259.08</td>
<td>141.77</td>
<td>0.54718</td>
</tr>
</tbody>
</table>

Since in practice it is not possible to calculate the values of parameters $r$ and $s$, if the value of $f_0$ is not known, then these values are calculated for an assumed value of $f_0=1$. It has no effect on the shape of the curve, because it depends on the $r/f_0$ ratio. For a calculated
Table V. Calculated values of thermoluminescence parameters

<table>
<thead>
<tr>
<th>No</th>
<th>Ic</th>
<th>Δc</th>
<th>Ec (eV)</th>
<th>dE/E (%)</th>
<th>(g(0) [e^{-}])</th>
<th>ds/s (%)</th>
<th>rc</th>
<th>dr/r (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.174</td>
<td>0.0334</td>
<td>2.408</td>
<td>-0.32</td>
<td>(1.23 \times 10^{23})</td>
<td>22.528</td>
<td>0.08697</td>
<td>-15.96</td>
</tr>
<tr>
<td>2</td>
<td>1.190</td>
<td>0.0637</td>
<td>0.399</td>
<td>0.16</td>
<td>(8.83 \times 10^{12})</td>
<td>-</td>
<td>0.01133</td>
<td>-13.28</td>
</tr>
<tr>
<td>3</td>
<td>1.110</td>
<td>0.0827</td>
<td>1.504</td>
<td>-0.26</td>
<td>(1.02 \times 10^{9})</td>
<td>-</td>
<td>0.00059</td>
<td>-18.38</td>
</tr>
<tr>
<td>4</td>
<td>1.064</td>
<td>0.0924</td>
<td>0.100</td>
<td>-0.04</td>
<td>(9.84 \times 10^{8})</td>
<td>-</td>
<td>0.00334</td>
<td>-11.49</td>
</tr>
<tr>
<td>5</td>
<td>1.015</td>
<td>0.1267</td>
<td>1.597</td>
<td>0.17</td>
<td>(9.63 \times 10^{4})</td>
<td>-</td>
<td>0.00072</td>
<td>27.74</td>
</tr>
<tr>
<td>6</td>
<td>1.105</td>
<td>0.1368</td>
<td>0.400</td>
<td>-0.08</td>
<td>(9.89 \times 10^{4})</td>
<td>-</td>
<td>0.02190</td>
<td>12.38</td>
</tr>
<tr>
<td>7</td>
<td>1.621</td>
<td>0.0842</td>
<td>1.503</td>
<td>-0.20</td>
<td>(5.91 \times 10^{6})</td>
<td>-</td>
<td>0.00801</td>
<td>-0.112</td>
</tr>
<tr>
<td>8</td>
<td>1.748</td>
<td>0.1390</td>
<td>0.400</td>
<td>-0.03</td>
<td>(6.97 \times 10^{4})</td>
<td>-</td>
<td>0.45418</td>
<td>-0.929</td>
</tr>
<tr>
<td>9</td>
<td>1.707</td>
<td>0.0919</td>
<td>0.100</td>
<td>-0.07</td>
<td>(1.02 \times 10^{7})</td>
<td>2.1384</td>
<td>0.54636</td>
<td>0.662</td>
</tr>
<tr>
<td>10</td>
<td>1.929</td>
<td>0.1260</td>
<td>1.596</td>
<td>0.25</td>
<td>(9.49 \times 10^{4})</td>
<td>-5.1196</td>
<td>0.88050</td>
<td>2.167</td>
</tr>
</tbody>
</table>

value of the kinetics order, one can select an \(r/f_0\) ratio, in order to obtain the curve shape which is the same as the shape of the experimental curve. The value of \(f_0=1\) is chosen, because, in this case, it is possible to calculate the value of the frequency factor. This is just one, of many possible solutions, for the given experimental curve, when the value of \(f_0\) is not known, and the value of kinetics order is between 1 and 2. In this way, the obtained solution, for parameter \(s\), has a minimum possible value, while for parameter \(r\), a maximum possible value. Physically this means that the actual value of parameter \(s\), is greater than the calculated value and the value of parameter \(r\) is lower.

Based on the calculated values of kinetic parameters of the process, it is possible to reconstruct the real physical process using differential equation models and calculated parameters. This allows examination of the kinetics of real TL phosphors. First, the glow curve corresponding to the model of ideal phosphor should be identified. This means that the curve should meet the requirements described in this paper. The conditions are that the glow curve has only one maximum and it needs to meet the criterion determined by the geometric parameters (shape factor and asymmetry factor), for a given value of parameter \(\Delta\). Among phosphors, which are used in dosimetry, TLD700H(\(\mathrm{LiF}:\mathrm{Mg,Cu,P}\)), TLD400(\(\mathrm{CaF}_2:\mathrm{Mn}\)) and TLD500(\(\mathrm{Al}_2\mathrm{O}_3:\mathrm{C}\)) are the closest to fulfilling the conditions. The tests proved that the dominant peak for TLD700H phosphor, approximately meets all requirements. The results are shown in Fig.1.

For typical glow curve of the dosimeter TLD700H [34] the same procedure of calculation is applied as well as the simulated glow curves. When the dominant peak is adjusted with GL function, the following values were obtained: \(T_m=482.75\), \(\omega = 19.58.8, z = 0.1259, z_1 = 2.79\times10^{-3}, z_2 = -4.99\times10^{-5}, b = -0.2722, b_1 = 8.56\times10^{-5}, \chi^2 = 1.32\times10^{-5}\). Then, values \(\omega_{eff} = 21.871, \delta_{eff} = 9.0078, \mu_s = 0.41187\) were calculated. Heating rate of phosphor was \(R=1\mathrm{K/s}\). Finally, values of TL parameter were calculated \(l_p = 1.145(1.15) \Delta_p = 0.0326(0.03245)\), \(E_p = 2.553 \mathrm{eV}(2.564), \Delta_p(0) = 5.53 \times 10^{25}, s^{-1}(7.11 \times 10^{25} \mathrm{s})\).
The obtained parameter values were substituted in the differential equation (3). The differential equation was solved numerically with these parameters to obtain the glow curve. The results are shown in Fig. 4. The figure shows that the glow curve completely coincides with the experimental curve. It can be concluded that the dominant peak of the glow curve, for TLD700H phosphor, may be described using kinetics of the model of ideal phosphor.

Fig. 4. Experimental TL glow curve for a TLD700H dosimeter (LiF: Mg, Cu, P) (solid line) and glow curve obtained by calculation using the model of ideal phosphor (solid square) (taken from paper [34])

9 Discussion

Application of GL functions to analyze TL curves with a maximum allows detection and quantification of changes in asymmetry and shape of the glow curve. Compared to the current glow curve analysis, based only on its asymmetry, GL functions allow definition of their type, i.e., how much they deviate from the pure form of Gaussian and Lorentz functions. First order kinetics is an exponential decay, and then the TL curve is an asymmetric Gaussian. Second order kinetics is a decay, which may be approximately described by the hyperbolic function. Since the glow curve of the second-order kinetics model, in the very beginning, has an exponential form, and in the second part, a hyperbolic form, then it can be described with a function, that is a combination of Gaussian and Lorentz functions. GL functions analysis confirms this fact fully.

Analysis of the model, that describes non-interactive kinetics, refers to glow curves

\[ r_p(0) = 0.07324(0.06776). \]
whose kinetic processes can be completed with first order kinetics or second order kinetics. Kinetics, at the end of the TL process, in case of the model of ideal phosphor \((m=0)\), is of the second order and in the case of a mixed-order model \((r=1)\) is of the first order. This means, that for the model of ideal phosphor, kinetics of the first order is an unstable process, while kinetics of the second order is stable. For the model of ideal phosphor, changes in the vicinity of kinetics of first order are faster and larger than in the vicinity of kinetics of the second order. Thereby, the shape and asymmetry of glow curves changed. For mixed-order kinetics, all this is opposite. This ensures that in the entire field of non-interactive kinetics, kinetic processes in models, of ideal phosphor, mixed order, and all the rest, belonging to non-interactive kinetics, can be mutually different.

When the model of TL relaxation is identified, based on an established criterion, it is necessary to calculate parameters of the TL process. This paper proposes a procedure for calculating the kinetic parameters for the simplest model. It is the model of ideal phosphor. A method for calculating parameters was based on the concept of kinetics order. The kinetics order parameter was defined by an equation, for which there is evidence that it will be valid for models that are part of the non-interactive kinetics model. These are models that have analytical solutions for corresponding differential equations (models of first, second, general and mixed order kinetics). The general order kinetics model can be treated as an approximation of the model of ideal phosphor. It has been assumed that the kinetics order parameter, is not characteristic of the TL process, but the glow curve is. In this way, variation of the value of kinetics order parameter during TL relaxation is avoided. The same procedures are used for the development of techniques for calculating the parameters of the model of ideal phosphor as in the case of calculating parameters for the general order kinetics model. The main task was to ensure that the obtained parameter values satisfied the differential equation of the model of ideal phosphor. In this way, the resulting solutions describe the physical process, and provide an assessment of the model.

The developed calculation method enables obtaining of the value of activation energy, with the relative error of calculation less than 0.5%. Values of the retrapping factor and frequency factor cannot be determined based on experimentally obtained glow curves. This would not be possible, unless the value of the filling factor is previously known even if there is an analytical solution of the differential equation. Therefore, a given glow curve has a great number of solutions. Any solution can be chosen, but it is convenient to choose a solution that allows the simplest analysis of the kinetic process, i.e. when the value of the filling factor is \(f_0=1\). This solution was chosen because it is valid for the limiting case and defines the limits of validity of the model. Changes in the value of \(\Delta\), for a range of values of \(l\) from 1 to 2, are very small and can be ignored. This is important, in order to obtain high calculation accuracy. Then it can be relatively easy to apply an empirical formula for calculating the frequency factor.

Criteria for assessing the kinetics model and algorithm for calculating the TL kinetic parameters, which are presented in this paper may be very useful in analyzing and un-
understanding the kinetics of the TL process. This is demonstrated by analysis of the three types of widely available and applied dosimeters. These dosimeters have commercial codes TLD400, TLD500 and TLD700H [10,16,26,27]. Glow curves of these dosimeters have dominant and isolated peaks. These peaks were analyzed and they originated only from one kind of traps. The results are very interesting and cannot be obtained by visual assessment. All three dosimeters have glow curves, which are visibly asymmetric. It has been estimated that these curves can be described with the general order kinetics model and kinetics order values between 1 and 2. If the values of the asymmetry factors are analyzed only, significant differences between the three curves cannot be identified. However, analysis of the values of the shape factor revealed important differences. The TLD700H dosimeter glow curve takes the form very similar to the curve of the model of ideal phosphor. This is quite unexpected, since in addition to the dominant peak there is a plurality of small peaks. These small peaks originated from other types of active traps and their impact on the dominant peak is negligible. The reason for this is that the small peaks are substantially smaller than the dominant peak, and the value of the retrapping factor for traps, from which the dominant peak arises, is very small. The glow curve of TLD500 corresponded to the model of non-interactive kinetics with a relatively high concentration of inactive traps. It may be noted that the value of the retrapping factor was greater than one, which means that the probability of retrapping was greater than the probability of luminescent recombination. However, because of the relatively high concentration of non-active traps, the glow curve takes a form, which can be described with the values of order kinetics between the 1 and 2. The TLD400 dosimeter has a low value of the retrapping factor, but not negligible. This value becomes more important when the active traps are more depleted. Also, the relatively low concentration of inactive traps has a significant influence on the shape of the curve when traps are less populated. It can be concluded that TL relaxation of the TLD400 dosimeter cannot be described with the model of ideal phosphor, or the mixed order kinetics model.

The analysis showed that the algorithm for calculating glow curve parameters, for the model of ideal phosphors, can be applied only to the dominant peak of the glow curve of the TLD700H dosimeter. In practice, kinetics parameters, in this case of phosphor, are often calculated using the first-order kinetics model or the general order kinetics model. Some authors, using deconvolution, proved that the shape of the dominant peak corresponds to the model of first order kinetics. As small peaks overlap with the dominant peak, it is possible, in the deconvolution process that such changes in shapes of small peaks will make the shape of the dominant peak correspond to the curve for the first order kinetics model. However, most authors reported that deconvolutions with a general order kinetic model obtained better compatibility with the experimental curve. Since the model of general-order kinetics is an approximation of the model of ideal phosphor, better accuracy and compatibility with the experimental curve is expected when the model of ideal phosphor is applied. The following values were obtained for kinetic models of the first order and general order, for the dominant
1. first order kinetics: \( l=1, E=2.229\text{eV}, \Delta=0.0373, s=3.56\times10^{26}\text{s}^{-1}, r=0, \)
2. general order kinetics: \( l=1.18, E=2.628\text{eV}, \Delta=0.0317, s(l)=3.54\times10^{26}\text{s}^{-1} \)

This analysis shows why, when using the model of general order kinetics, accurate results, or very approximate, or incorrect with a relatively large error, can be obtained. The general order kinetics model is designed to simply and as accurately as possible describe the asymmetry of the curves. If the experimental glow curve coincides, in shape, with the glow curve formed based on this model, then the values of the calculated parameters will be accurate. If these shapes differ slightly, then, in the fitting process, the calculated parameter values shift slightly, in order to correct for variations in the value of the shape factor. If the difference between the shape factor of the theoretical glow curve and its actual value is greater, deviation from the exact value of TL parameters will be higher.

10 Conclusions

In this paper a completely new method for calculating the kinetic parameters of the process relating to TL relaxation in ideal phosphors was developed. This process is close to real situations as it relates to the model with realistic physical parameters.

A method for calculating the parameters of TL relaxation for the model of ideal phosphors is based on the concept of kinetics order. The kinetics order is defined by an equation applied to models of the first, second, general and mixed order kinetics. The new definition includes also a new meaning for the parameter of kinetics order. The kinetics order, in this case, cannot be understood as a parameter that defines the TL process, but as a parameter that determines the glow curve.

Using the GL asymmetric function, it was revealed that the dominant peak of a TLD700H \((\text{LiF:}\text{Mg,Cu,P})\) dosimeter, could be described by the model of ideal phosphors. The values of physical parameters, which determine the kinetics of TL were evaluated based on the method for calculating parameters of the model of ideal phosphor. Values of the retrapping factor, frequency factor and activation energy were calculated for the assumed value of the filling of traps of \( f_0=1 \). The resulting glow curve coincided with the experimental curve.

References

Glow Curve Analysis and Calculation of Thermoluminescence Parameters


