

NEW FITTING ALGORITHM FOR THE DETERMINATION OF TRAP PARAMETERS FROM TL CURVES

A. Mandowski and J. Świątek

Institute of Physics, Pedagogical University ul. Armii Krajowej 13/15, 42–200 Częstochowa, Poland

Abstract — Many applications are based on the analysis of thermoluminescence (TL) glow curves. For these purposes, relatively simple but credible methods are required. In this paper a new fitting algorithm is presented for determination of the activation energy and other physical trap parameters from TL peaks. The fitting method was derived directly from the simple model. The algorithm allows the analysis of a single TL peak, as well as the deconvolution of complex TL curves. Using numerically generated TL spectra preciseness and stability of the algorithm are studied. The results are compared with the classical fitting techniques based on the general order kinetics model. It is shown that the novel method is faster and in many cases gives more reliable results.

INTRODUCTION

Computerised glow curve analysis is widely used for determining trap parameters from TL (thermoluminescence) curves as well as for dosimetric applications^(1,2). Numerical fitting of a series of peaks allows deconvolution of complex TL spectra. The most popular analytical expression used for these purposes is the Randall–Wilkins (RW) approximation⁽³⁾ where TL intensity J is given by the following equation:

$$J = \chi v n_0 \exp\left(\frac{-E}{kT}\right) \exp\left[-\frac{v n_0}{\beta} \int_{T_0}^T \exp\left(\frac{-E}{kT'}\right) dT'\right]. \quad (1)$$

This solution is known as first order or monomolecular kinetics. It was found that many observed TL curves obey this simple equation⁽⁴⁾. To include more complex TL processes, May and Partridge⁽⁵⁾ suggested adding an additional parameter — the kinetic order b . They assumed that the intensity J is given by simple differential equation:

$$J/\chi = -\dot{n} = v n^b \exp\left(\frac{-E}{kT}\right) \quad (2)$$

For $b = 1$ it is equivalent to the RW solution (Equation 1). Later, the general order (GO) kinetics model was developed by Chen⁽⁶⁾ and other authors. In the above equations n denotes concentration of charge carriers in traps, T is the temperature of the sample, k is the Boltzmann constant, β is the heating rate and n_0 denotes the initial concentration of charge carriers in traps at the temperature T_0 . The GO model has become very popular in practical applications due to its simplicity and good description of the shape of TL curves. Nevertheless, it is also criticised by many authors due to the non-physical character of the parameter b . The model is physically justified only in two limiting cases: $b = 1$ that corresponds to the RW model and $b = 2$ derived by Garlick and Gibson⁽⁷⁾ (second order or bimolecular kinetics). Moharil⁽⁸⁾ and Opanowicz⁽⁹⁾ pointed out that the kinetic

order is usually non-constant during a thermally stimulated process and should not be used for characterisation of TL. Lewandowski *et al.*⁽⁴⁾ suggest using a kinetic order function instead of the kinetic order constant. It will be shown in this paper that in some cases the application of the GO model gives wrong results with errors in estimation of the activation energy of more than 50%.

The above arguments lead to a search for other physically acceptable models. Recently, Mandowski and Świątek⁽¹⁰⁾ suggested using other equations that can be written in the form of the ‘corrected initial rise’ method. It was proved numerically, that the validity of this approximation is not limited only to an initial part of a TL peak, but usually covers the whole measurable TL curve. The first approximation is:

$$\frac{-E}{kT(t)} = \ln[\mathcal{L}(t)] + \ln\left\{\frac{1}{M + \mathcal{U}_\infty - \mathcal{U}(t)} \left[\frac{1}{\mathcal{U}_\infty - \mathcal{U}(t)} + L_1\right]\right\} + \ln(L_2) \quad (3)$$

where M denotes the concentration of electrons in deep traps and constants L_1 and L_2 are defined by

$$L_1 = \frac{B - A}{AN + BM} \quad (4)$$

and

$$L_2 = \frac{AN + BM}{vB} \quad (5)$$

The variables \mathcal{L} and \mathcal{U} are defined as follows:

$$\mathcal{L}(t) \equiv -\dot{m}(t) \quad (6)$$

$$\mathcal{U}(t) \equiv \int_0^t \mathcal{L}(t') dt' = m_0 - m(t) \quad (7)$$

where m denotes the concentration of holes in recombination centres, N denotes the concentration of traps, A and B denote trapping and recombination coefficients, respectively, and $\mathcal{U}_\infty = n_0$. \mathcal{L} and \mathcal{U} are directly pro-

portional to the observed TL intensity J and the area under the TL curve respectively. It can be shown that Equation 3 is mathematically equivalent to a well-known quasi-equilibrium (QE) approximation of Kelly and Bräunlich⁽¹¹⁾ when deep trap levels are also taken into account. With all its simplicity and accuracy this method can be used only to analyse a single, well separated peak. Moreover, the knowledge of M , L_1 and L_2 does not allow a direct calculation of the dependence $J(T)$. Therefore Equation 3 cannot be applied to curve fitting and deconvolution. In this paper it is shown how to construct an algorithm, based on Equation 3, that would be able to calculate $J(T)$ and then to determine trap parameters by using a curve fitting method.

THEORY

Let us define new normalised variables for the TL intensity, the peak area and other symbols:

$$j(t) = \mathcal{L}(t)/n_0 \quad (8)$$

$$u(t) = \mathcal{U}(t)/n_0 \quad (9)$$

$$r = A/B \quad (10)$$

$$\eta_0 = n_0/N \quad (11)$$

$$\mu_0 = M/n_0 \quad (12)$$

$$\epsilon(t) = \exp\left(-\frac{E}{kT(t)}\right) \quad (13)$$

Now, Equation 4 may be written:

$$j(t) = \frac{v\epsilon(t)[\mu_0 + 1 - u(t)][1 - u(t)]}{\mu_0 + r/\eta_0 + (1 - r)[1 - u(t)]} \quad (14)$$

In trying to construct an effective fitting algorithm based on this equation we are faced with two problems. Firstly, the number of parameters has to be reduced. Preferably, the number should not be greater than four per peak. Secondly, the method of calculating $j(t)$ has to be fast enough. Best results would be achieved if $j(t)$ had an analytical form. However, mathematically, Equation 14 is a non-linear integral equation with respect to $j(t)$.

To reduce the number of parameters let us rewrite Equation 14 in the form:

$$j(t) = \frac{v\epsilon(t)[1 - u(t)]}{1 - r[1/\eta_0 + 1 - u(t)][\mu_0 + 1 - u(t)]^{-1}} \quad (15)$$

There are several limiting conditions that can be taken into account. Here, as an example we will consider the case of a high concentration of deep traps as compared to initially trapped charge carriers, i.e. $\mu_0 \gg 1$. In this case the equation reduces to:

$$j(t) = \frac{v'\epsilon(t)[1 - u(t)]}{1 + r'u(t)} \quad (16)$$

where

$$v' = \frac{v}{1 + r/\mu_0(1/\eta_0 - 1)} \quad (17)$$

$$r' = \frac{r/\mu_0}{1 + r/\mu_0(1/\eta_0 - 1)} \quad (18)$$

Hence, the TL intensity $J(t)$ depends on four parameters: E , v' , r' and χ . It should be noted that for $r' = 0$ the equation reduces to well known RW (i.e. first order) approximation. Now, we discuss the method of calculation of $j(t)$. Assume that the fitting algorithm requires computation of $(k_{\text{end}} + 1)$ values $j_k = j(t_k)$ for equidistant time intervals $\Delta t = t_{k+1} - t_k$. It is obvious to assume $j_0 = 0$ and $u_0 = u(t_0) = 0$. Then, subsequent values are calculated from the equation:

$$j_k = \frac{v'\epsilon_k(1 - u_k)}{1 + r'u_k} \quad (19)$$

The key point is the method of estimation of u_k . Below, four formulae are suggested:

(i) u_k not approximated

$$u_k = u_{k-1} \quad (20)$$

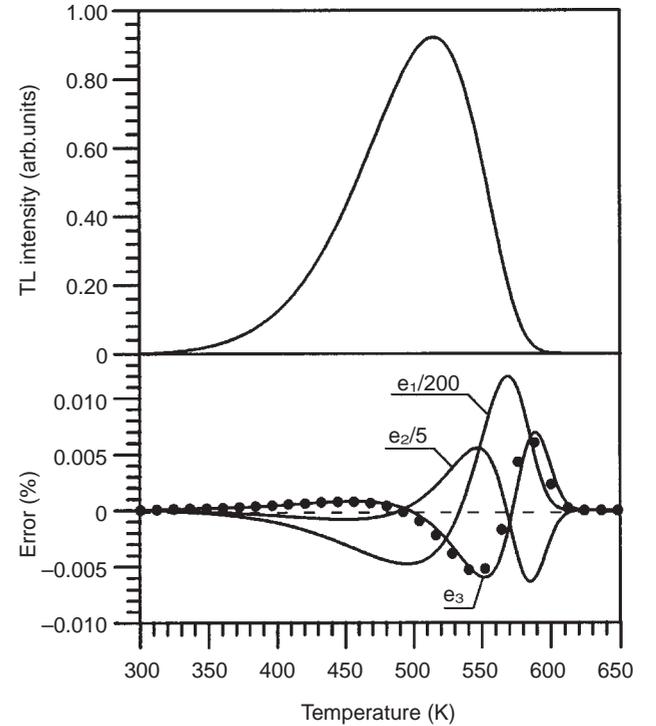


Figure 1. The comparison of the accuracy of computing a TL curve by using the four methods (Equations 20–24) and Equation 16. These methods are represented by curves e_1 , e_2 and e_3 respectively. The filled circles (●) represented the most accurate, last method (Equation 23). To fit on the diagram, the errors calculated for (i) and (ii) were reduced by a factor of 200 and 5 respectively. The spectra were calculated using the following parameters: $E = 0.9$ eV, $v' = 10^{10}\text{s}^{-1}$, $r' = 10^3$ and the heating rate $\beta = 1$ K.s⁻¹. The computation step $\Delta t = 1$ s; one iteration.

(ii) rectangular approximation

$$u_k = u_{k-1} + j_{k-1} \Delta t \quad (21)$$

(iii) trapezoidal approximation with derivative estimation

$$u_k = u_{k-1} + \frac{j_{k-1} - j_{k-2}}{2} \Delta t \quad (22)$$

(iv) trapezoidal approximation

$$u_k = u_{k-1} + \frac{j_k - j_{k-1}}{2} \Delta t \quad (23)$$

For the first three methods (i–iii) the variable u_k needs to be corrected as follows:

$$u_k^{(2)} = u_{k-1} + \frac{j_k^{(1)} - j_{k-1}}{2} \Delta t \quad (24)$$

where $j_k^{(1)}$ denotes the previously calculated intensity. Using these methods the process of calculating j_k and then correcting u_k may be repeated many times to increase accuracy. Using the last method (iv) one needs to calculate j_k by solving a quadratic equation.

NUMERICAL CALCULATIONS

Each of the methods suggested (i–iv) turned out to be very effective and convergent. However there are huge differences in accuracy. The least effective is the method (i) which requires some correcting iterations

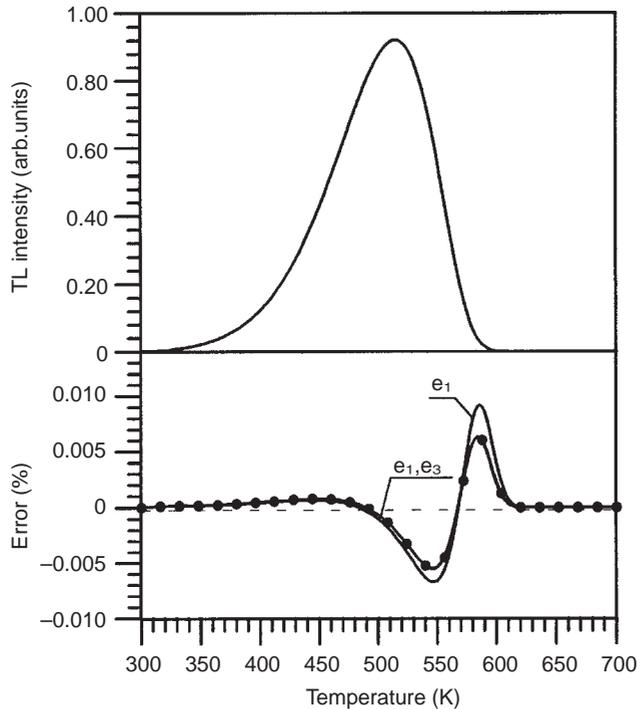


Figure 2. Illustration of the influence of the step of calculations Δt on the accuracy of the computation of TL curve. The calculations were performed for the method (iv) using the same set of parameters as for Figure 1 except the computation step Δt .

(see Figure 1 to give reasonable results. The best are the two last methods (iii–iv) whose accuracy depends only on the time interval Δt . The dependence for the last method is illustrated in Figure 2. As can be seen in the first two figures the calculation errors are mainly accumulated in the descending part of the TL peak. However, even for very high steps of Δt the correctness of calculating TL intensity is excellent. When applied to a fitting program it allows the use of high steps at the beginning of the calculations and then, when a first approximation is achieved, Δt may be decreased to get the best accuracy. In each of the figures presented the error was defined as $(J_{\text{theoretical}} - J_{\text{fit}})/J_{\text{max}}$.

To show the usefulness of the method proposed, a fitting program was constructed based on Equation 16. Therefore, its range of applicability is limited to the case of high concentrations of deep traps compared to the initially trapped charge carriers, i.e. $\mu_0 \gg 1$. The program was applied to the analysis of numerically generated TL curves that were computed by solving the basic set of differential equations (i.e. the simple model⁽⁷⁾). The results are compared with classical analysis performed by using the GO kinetics model defined by Equation 2. In Table 1 four examples of the analysis are presented. The generated curves were calculated using common parameters: $E = 0.9$ eV, $\nu = 10^{10} \text{ s}^{-1}$, $r = 10^4$,

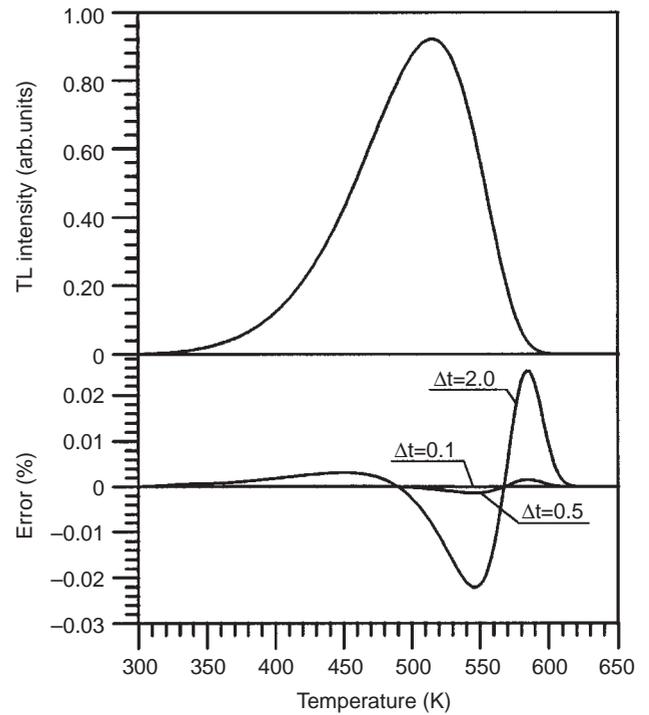


Figure 3. Application of GO model and QE approximation (Equation 16) for fitting to a numerically generated TL curve. The TL curve represented by open circles (○) was calculated by solving the basic set of differential equations using the following parameters: $E = 0.9$ eV, $\nu = 10^{10} \text{ s}^{-1}$, $r = 10^4$, $N = 10^{15} \text{ cm}^{-3}$, $B = 10^{-11} \text{ cm}^3 \cdot \text{s}^{-1}$, $\mu_0 = 10^2$ and $\eta_0 = 1.0$. For the fitted parameters see Table 1 (curve 2).

$N = 10^{15} \text{ cm}^{-3}$, $B = 10^{-11} \text{ cm}^3 \cdot \text{s}^{-1}$. The first example shown was calculated for $\mu_0 = 11$ and $\eta_0 = 0.9$. In this case the GO model does not describe the shape of the curve correctly. Best fit was attained for the kinetic order $b = 0.93$. The fitted energy is much lower than expected, $E = 0.52 \text{ eV}$. Using the simplified quasi-equilibrium model (Equation 16) we get a reasonable approximation, $E = 0.87 \text{ eV}$. The second example also presented in Figure 3 was calculated for $\mu_0 = 100$ and the full initial filling of traps $\eta_0 = 1.0$. In this case the GO model characterises the shape of the curve quite well using a very low kinetic order $b = 0.78$: however, it estimates the activation energy as low as $E = 0.44 \text{ eV}$. Applying the new algorithm we get the correct value, $E = 0.90 \text{ eV}$. It should be noted that for low initial filling ratios $\eta_0 \ll 1$ the results obtained from GO and QE usually coincide. Such examples are presented in Table 1, curves 3 and 4. In these cases the advantage of using the QE model instead of the GO is that we get information on the parameters v' and r' which have clear physical meaning instead of information on the formal parameter b .

DISCUSSION

In this paper a method was presented of applying a simplified version of the QE model to the analysis of TL data in the case of high concentration of deep traps, $\mu_0 \gg 1$. It was shown that the algorithm is very efficient and allows one to calculate TL curves with a high computing step. Unlike the classical RW and GO models it does not require calculation of the integral appearing in the Equation 1, consequently it is very fast. The explicit integration is replaced by one of the iteration methods (Equations 20–23). The advantages of using the QE model instead of GO kinetics are indisputable. First of all one uses a physical model having all its parameters clearly defined. Furthermore, its accuracy is much better and is justified numerically⁽¹⁰⁾. Although the fitting program was constructed for the exemplary approximation (Equation 16), one should note that the same methods may be used for any other approximation derived from (Equation 15) as well as for the basic QE equation itself. However, in every case its effectiveness should be tested numerically.

Table 1. The comparison of the parameters used for the calculation of TL glow curves using the simple model (input parameters) with those fitted by the GO model and QE model (Equation 16). Other parameters common for all curves: $v = 10^{10} \text{ s}^{-1}$, $r = 10^4$, $N = 10^{15} \text{ cm}^{-3}$, $B = 10^{-11} \text{ cm}^3 \cdot \text{s}^{-1}$.

	Input parameters					GO fit (Equation 3)		QE fit (Equation 18)		
	E (eV)	μ_0	η_0	r'	v'	E (eV)	b	E (eV)	r'	v'
Curve 1	0.9	11	0.9	8.9	9.8×10^7	0.52	0.93	0.87	8.0	5.3×10^7
Curve 2 (Fig. 3)	0.9	10^2	1.0	10^2	10^{10}	0.44	0.78	0.90	96	9.2×10^9
Curve 3	0.9	10^3	0.1	0.11	1.1×10^8	0.88	1.02	0.90	0.11	1.1×10^8
Curve 4	0.9	10^4	0.01	0.01	10^8	0.90	1.00	0.90	0.01	1.0×10^8

REFERENCES

- Bos, A. J. J., Piters, T. M., Gomez Ros, J. M. and Delgado, A. *GLOCANIN: An Intercomparison of Glow Curve Analysis Computer Programs*. IRI-CIEMAT Report 131-93-005 (IRI, Delft, The Netherlands) (1993).
- Horowitz, Y. S. and Yossian, D. *Computerised Glow Curve Deconvolution: Application to Thermoluminescence Dosimetry*. Radiat. Prot. Dosim. **60**(1), 1–114 (1995).
- Randall, J. T. and Wilkins, M. H. F. *Phosphorescence and Electron Traps: I. The Study of Trap Distributions*. Proc. R. Soc. A **184**, 366–389 (1945).
- Lewandowski, A. C., Markey, B. G. and McKeever, S. W. S. *Analytical Description of Thermally Stimulated Luminescence and Conductivity without the Quasiequilibrium Approximation*. Phys. Rev. B **49**, 8029–8047 (1994).
- May, C. E. and Partridge, J. A. *Thermoluminescence Kinetics of Alpha-irradiated Halides*. J. Chem Phys. **40**(5), 1401–1409 (1964).
- Chen, R. *Glow Curves with General Order Kinetics*. J. Electrochem. Soc. **116**, 1254–1257 (1969).
- Garlick, G. F. J. and Gibson, A. F. *The Electron Trap Mechanism of Luminescence in Sulphide and Silicate Phosphors*. Proc. R. Soc. London, Sect. A **60**, 574 (1948).
- Moharil, S. V. *On the Variation of Order of Kinetics during Thermoluminescence*. Phys. Status Solidi a **68**, 413–418 (1981).
- Opanowicz, A. *On the Kinetics Order of Thermoluminescence in Insulating Crystals*. Phys. Status Solidi a **116**, 343–348 (1989).
- Mandowski, A. and Świątek, J. *Determination of Trap Parameters from Generalised Initial Rise Equations*. Radiat. Prot. Dosim. **65**(1–4), 55–58 (1995).
- Kelly, P. and Bräunlich, P. *Phenomenological Theory of TL*. Phys. Rev. B **1**, 1587 (1970).