INVESTIGATION OF PHOSPHORESCENCE DECAY USING TL–LIKE PRESENTATION

R. Chen and N. Kristianpoller
School of Physics and Astronomy
Raymond and Beverly Sackler Faculty of Exact Sciences
Tel Aviv University, Tel Aviv 69978, Israel

Abstract — The phosphorescence decay of radiation stimulated luminescent materials at a constant temperature reveals information on the processes involved. The shape of the decay curve depends on the kinetics. Inversely, a study of these curves yields information on the kinetic parameters. A way of presenting the phosphorescence decay which emphasises the features of the curve is to plot $y=t\cdot I(t)$ as a function of $x=\ln t$. This yields a peak shaped curve for a simple phosphorescence decay. This curve resembles the TL glow curve that one expects for the same kinetic law. In the present work, the shape of the curve is studied by checking the symmetry factor $\mu_g = \delta/\omega$ where $\delta=x_2-x_m$, $\omega=x_2-x_1$ and where x_m is the maximum point and x_1, x_2 are the two half-intensity points. The dependence of μ_g on the kinetic order b is determined. Inversely, the parameter b can be evaluated from the experimental results.

INTRODUCTION

The study of phosphorescence, namely, the long period decay of luminescence at constant temperature has been accompanying the research into thermoluminescence. The pioneering work of Randall and Wilkins[1], which is considered by many as the cornerstone of the modern investigation of TL, included an extensive discussion on phosphorescence decay. In a sense, the study of phosphorescence is expected to be simpler than that of TL. In the latter, while scanning through temperature, the probability is large of going from a range where one trapping state is being thermally emptied, into another range where another kind of trap is dominating. When a measurement is made at a constant temperature, it is more likely that fewer trapping states (hopefully exactly one) are involved in the process. Thus, the task of extracting trapping parameters from a decay curve looks, at least in principle, simpler than that of analysing TL peaks. On the other hand, the decay curves are usually slowly varying ones and no outstanding features can be seen, which reduces our ability to extract the relevant parameters from the results. Randall annd Wilkins[1] themselves hinted at the solution of this problem and suggested that plotting $y=t\cdot I(t)$ as a function of $x=\ln t$ should yield a curve which would accentuate the hidden features of the decay curve in hand. Visocekas[2] further studied this representation and showed that both in first order cases and in general order ones (including second order kinetics), a peak should occur which resembles to some extent a TL peak. The dependence of the shape of this peak on the order of kinetics also resembles that of TL, as will be

elaborated below. These peaks shift with temperature and, as shown by Visocekas[2,3], one can evaluate the activation energy E by measuring the shift Δ (on the ln t scale) at two temperatures T_1 and T_2.

The expression given is

$$E = \Delta k\, T_1 T_2/(T_2-T_1) \tag{1}$$

The purpose of the present work is to discuss further this presentation of phosphorescence decay, to show its similarity to TL peaks with hyperbolic heating rates and to indicate a way of extracting directly the kinetics order from this representation. It is to be noted that this approach bears some resemblance, at least in principle, to a very recent work[4] describing a new method, Photoluminescence Transient Spectroscopy (PTS) which is similar to the well known DLTS method. This involves measuring the luminescent intensity of a fast exponentially decaying process, at two different instants of time and looking for the occurrence of peaks when the differential luminescent intensities are plotted as a function of T.

FIRST ORDER KINETICS

The very well known first order equation can be written as

$$I = -dn/dt = n/\gamma \tag{2}$$

where I is the phosphorescence intensity, n is the instantaneous concentration of trapped carriers (m^{-3}), t the time(s) and $\gamma=s^{-1}\exp(E/kT)$ where s is the frequency factor(s), E is the activation energy (eV), k is Boltzmann's constant $(eV.K^{-1})$ and T is the absolute temperature (K). γ is the characteristic lifetime of the

443

process, namely the time for the decay of the intensity to e^{-1} of its initial value. It is obvious that γ depends very strongly on the temperature. Thus, if we take $T_2 > T_1$ we get $\gamma_1 > \gamma_2$.

The solution of Equation 2 at a given temperature is

$$I = I_o \exp(-t/\gamma) = (n_o/\gamma) \exp(-t/\gamma) \qquad (3)$$

Let us take a new variable $x = \ln t$, i.e. $t = e^x$. We now have

$$I = I_o \exp(-e^x/\gamma) \qquad (3')$$

If we now take $y = I \cdot t$, we have

$$y = I_o e^x \exp(-e^x/\gamma) \qquad (4)$$

This represents a peak shaped curve, similar to a TL peak. For low values of x, $\exp(-e^x/\gamma)$ is nearly constant, and the e^x behaviour in the first exponent dominates. At higher values of x, the decreasing function $\exp(-e^x/\gamma)$ takes over and for large values of x, y goes to zero. In between, a maximum occurs, the location of which, x_m, can be found by equating the derivative of Equation 4 to zero. This immediately yields the maximum condition

$$\exp(x_m) = \gamma \to t_m = \gamma \to \ln t_m = \ln \gamma \qquad (5)$$

Thus, plotting $y = I \cdot t$ against $x = \ln t$ yields a peak having a maximum at $x_m = \ln \gamma$. In fact, since $\ln t$ is a monotonic function, the maximum would occur at $t_m = \gamma$ even if $t \cdot I(t)$ is plotted against the time t directly. The rest of the discussion, however, is related to the specific plot of y against $x = \ln t$.

As shown by Visocekas[3], if the phosphorescence decay associated with the trapping states is performed at two different temperatures T_1 and T_2, the maxima in the $I \cdot t$ against $\ln t$ plot will occur at the points $t_1 = \gamma_1 = s^{-1} \exp(E/kT_1)$; $t_2 = \gamma_2 = s^{-1} \exp(E/kT_2)$; respectively. The shift with temperature on the $\ln t$ scale would be

$$\Delta = \ln \gamma_1 - \ln \gamma_2 = (E/k)(1/T_1 - 1/T_2) \qquad (6)$$

from which E is readily found as pointed out in Equation 1 above. Once E is found, s can be evaluated immediately using a known value of γ at a certain temperature T.

Since the curve obtained is similar to that of TL, there is a point in studying its symmetry properties using tools developed for the study of TL. We shall therefore try to evaluate, in addition to the value of x_m mentioned above, the magnitudes x_1 and x_2, the two points at which $y(x)$ reaches half of its maximum intensity. Inserting the value of x_m into Equation 4, we get

$$y_m = I_o \exp(x_m) e^{-1} = (n_o/\gamma) \gamma e^{-1} = n_o/e \qquad (7)$$

x_1 and x_2 will be the low and high solutions of $y = y_m/2$, namely, of

$$n_o/(2e) = (n_o/\gamma) e^x \exp(-e^x/\gamma) \qquad (8)$$

Defining $Z = e^x/\gamma$ we get the equation

$$Z e^{-z} = 1/(2e) \qquad (8')$$

The solutions Z_1 and Z_2 can obviously be found, irrespective of γ. Denoting by Z_1 and Z_2, $(Z_2 > Z_1)$, the two solutions, we immediately get $x_1 = \ln(\gamma Z_1)$; $x_2 = \ln(\gamma Z_2)$; $x_m = \ln \gamma$. Following the study of TL[5,6] we now define the quantities

$$\omega = x_2 - x_1 = \ln(\gamma Z_2) - \ln(\gamma Z_1) = \ln(Z_2/Z_1)$$

$$\tau = x_m - x_1 = \ln \gamma - \ln(\gamma Z_1) = -\ln Z_1 (>0) \qquad (9)$$

$$\delta = x_2 - x_m = \ln(\gamma Z_2) - \ln \gamma = \ln Z_2$$

In the same way as in the TL convention, we define the symmetry factor usually denoted μ_g, $\mu_g = \delta/\omega$. Substituting from Equations 9 we get

$$\mu_g = \ln Z_2/\ln (Z_2/Z_1) \qquad (10)$$

A small computer program has been prepared which found the two roots of Equation 8' and evaluated the value of μ_g for the first order case to be $\mu_g = 0.4026$. It is to be noted that this is the value of μ_g for the first order case, irrespective of the value of the frequency factor s and the activation energy E.

GENERAL ORDER KINETICS

The kinetic equation known as 'general order' is

$$I = -dn/dt = s' \exp(-E/kT)n^b \qquad (11)$$

where b is the kinetic order and s' a constant pre-exponential factor with the dimensions $m^{3(b-1)}.s^{-1}$. This includes, of course, the special case $b = 2$, namely, the second order kinetics where the dimension of s' is $m^3.s^{-1}$. Let us define a frequency factor $s = s'n_o^{b-1}$ having units of s^{-1}; the solution of Equation 11 is now

$$I = sn_o \exp(-E/kT)/[1+(b-1)s \exp(-E/kT)t]^{b/(b-1)} \quad (12)$$

Defining as above $\gamma = s^{-1} \exp(E/kT)$ and changing the variables so that $x = \ln t \to t = e^x$ and $y = I \cdot t$, we get

$$y = (n_o/\gamma)e^x/[1+(b-1)e^x/\gamma]^{b/(b-1)} \qquad (13)$$

The maximum condition is found, again, by setting $dy/dx = 0$ which yields $\exp(x_m) = \gamma \to x_m = \ln(t_m) = \ln \gamma$. A change in the temperature would, therefore, cause the same kind of shift of the maximum, and the method by Visocekas[2] to evaluate E and s can be applied with no change.

Inserting the maximum condition into Equation 13 we get $y_m = n_o/b^{b/(b-1)}$ which, for the special case of $b = 2$ yields $y_m = n_o/4$. Following the procedure described above for the first order case, we would like to find the lower and higher values of x which solve the equation $y = y_m/2$ where y is given in Equation 13. Using again the variable $Z = e^x/\gamma$, we get the equation

$$2Z = \{[1+(b-1)Z]b^{-1}\}^{b/(b-1)} \qquad (14)$$

444

Equation 14 is independent of E and s' and therefore, the values Z_1 and Z_2 will depend only on b. A computer program has been prepared which solves Equation 14 for any given b (excluding b=1 which has been dealt with above). Once Z_1 and Z_2 are found, the values of τ, δ, ω and μ_g can be evaluated using Equations 9 and 10. Figure 1 depicts the curve of μ_g plotted against b thus calculated for $1 \leqslant b \leqslant 3$. The main use of Figure 1 should be the following. Given a decay curve, plot l·t against ln t, evaluate the symmetry factor μ_g and then use Figure 1 to find the effective order of the process.

The special case of second order kinetics deserves some attention. Equation 14 reduces to

$$8Z = (1+Z)^2 \qquad (15)$$

the solutions of which are $Z_1 = 3 - 2\sqrt{2}$ and $Z_2 = 3 + 2\sqrt{2}$. From this we readily get $\tau = -\ln Z_1 = 1.7627$, $\delta = \ln Z_2 = 1.7627$ and $\mu_g = 0.5$, namely, the resulting curve is exactly symmetric.

DISCUSSION

A method which transforms decay curves into peak shaped ones has been described, which emphasises the features of the decay curves. Simple methods for evaluating the activation energy, frequency factor and kinetics order have been discussed. A mention should be made of the fact that Figure 1 which shows the dependence of the shape factor μ_g on the kinetics order b, is rather similar to the figure given previously[6] for the dependence of μ_g on b for the TL peaks obtained under a linear heating function. The main difference between the two is that in the present case, the curve of μ_g as a function of b is one-valued whereas in the linear heating TL case, there is a slight dependence of μ_g on E and s for any given value of b. In this sense, the present case resembles TL peaks with a hyperbolic heating function[3,7,8] and Figure 1 can be utilised for the analysis of TL curves under this heating schedule as well.

Finally, although Equation 11 is termed 'general order', it includes only three parameters, whereas in the most general case (see discussion in Chen and Kirsch[3]), a single TL peak depends on eight free parameters. The method described herewith should
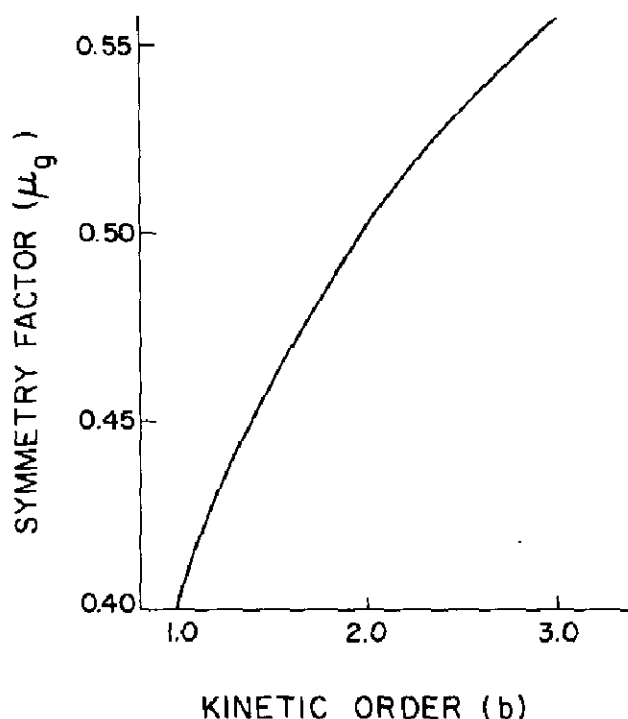

KINETIC ORDER (b)

Figure 1. The symmetry factor μ_g as a function of the order b, calculated from Equations 8' and 14.

be checked with real-life decay curves as well as with computer generated curves found by the numerical solution of the three simultaneous differential equations governing the TL resulting from the thermal release of carriers from a single trapping state and their subsequent recombination into a single kind of centre. In this respect, we mention that it has recently been shown[9] that the 3-parameter approximation is not a good representation for a more complicated case of simultaneous release of electrons and holes. The latter involves, however, four simultaneous equations with more parameters, including (which is most relevant to the complication of this situation) two activation energies which are active in the same temperature range. The three parameter approximation is expected to be valid in the 'usual' case where either electrons or holes are thermally released in a given temperature range.

REFERENCES

1. Randall, J. T. and Wilkins, M. H. F. *Phosphorescence and Electron Traps II. The Interpretation of Long Period Phosphorescence.* Proc. R. Soc. London A **184**, 390-407 (1945).

2. Visocekas, R. *La Luminescence de la Calcite après Irradiation Cathodique: TL et Luminescence par Effet Tunnel.* Thèse, Université Pierre et Marie Curie, Paris, p. 259 (1978).

3. Chen, R. and Kirsh, Y. *Analysis of Thermally Stimulated Processes.* (Oxford: Pergamon Press) p. 361 (1981).

4. Teh. C. K., Tin C. C. and Weichman, F. L. *A New Method of Analysis of Photoluminescence Decay Curves.* J. Lumin. **35**, 17-23 (1986).

5. Halperin, A. and Braner. A. A. *Evaluation of Thermal Activation Energies from Glow Curves.* Phys. Rev. **117**, 408-415 (1960).

6. Chen, R. *On the Calculation of Activation Energies and Frequency Factors from Glow Curves.* J. Appl. Phys. **40**, 570-585 (1969).

7. Kelly. P. J. and Laubitz, M J. *On the Analysis of Glow Curves.* Can. J. Phys. **45**, 311-321 (1967).

8. Christodoulides. E. *Parameter Determination for General Order TL Peaks Measured with Hyperbolic Heating.* Phys. Status Solidi a **94**, 251-258 (1986).

9. McKeever. S. W. S., Rhodes. J. F., Mathur. V. K., Chen. R., Brown, M. D. and Bull. R. K. *Numerical Solutions to the Rate Equations Governing the Simultaneous Release of Electrons and Holes during TL and Isothermal Decay.* Phys. Rev. **32**, 3835-3843 (1985).