On the Initial Rise Method for Kinetic Analysis in Thermally Stimulated Luminescence

Mahua Karmakar

Department of Physics, Acharya Prafulla Chandra College, New Barrackpore, 24 *Parganas (N),*
*West Bengal-*700 131 *,India*
mahua_apc@yahoo.com

Abstract

Several methods are known for the evaluation of the main kinetic parameters related to a thermally stimulated luminescence popularly known as thermoluminescence (TL). Among them Initial rise method is known as the simplest experimental procedure to obtain the activation energy. In this paper, a critical appraisal of the works on Initial rise and related methods in the literature is made. In spite of some inherent difficulties the method has been extensively used because of its very weak dependence on the order of kinetics.

**Keywords:** Thermoluminescence, Initial rise method, Activation energy, Order of kinetics.

1. Introduction

Thermoluminescence (TL) occurs when a solid sample (usually an insulator or semiconductor) is heated after being irradiated at lower temperature T_0 . Part of the energy absorbed by the sample in course of irradiation might be released during heating. Thermoluminescence has found important applications in dating and dosimetry (Chen and McKeever, 1997). The rigorous theory of thermoluminescence is very complicated. The most popular model of thermoluminescence (TL) is the three parameter model(Chen & McKeever , 1997) extensively developed by Chen (1969a; 1969b)In three-parameter model , TL is described by the three parameters namely activation energy (E), order of kinetics (b) and frequency factor (s) . Recently there has been a plethora of published papers dealing with methods by which trapping parameters (mainly E and s) can be obtained from a glow curve. Number of methods such as Peak shape method, Initial Rise method, Various heating rates method, Curve-fitting method have been adopted by various research workers(Chen & McKeever, 1997). Initial rise (IR) method suggested by Garlick and Gibson(1948) is the simplest experimental procedure to obtain the trap depth and is nearly independent of the kinetics involved. In this paper we present a brief review of the works on initial Rise method for the determination of trapping parameters of TL peak.

1.1 Critical appraisal of the literature on IR and related methods

The geometrical shape of a TL glow peak plays an important role in calculating trapping parameters. In IR method, the initial rise portion of the peak i.e., $T < T_m$ (where T_m is the temperature at which the TL maxima occurs) is taken under consideration. In the low initial rise tail of a peak, the amount of trapped electrons can be assumed to be a constant , the dependence of temperature being negligible .The initial part of TL curve is exponentially dependent on temperature according to $I(T) = cons \tan t \times \exp(-E/kT)$ Fig. 1 shows the initial -rise part of a single glow peak .

Fig.1. *The initial-rise part of a glow peak of* $I_c \leq 15\%$ *of* T_M
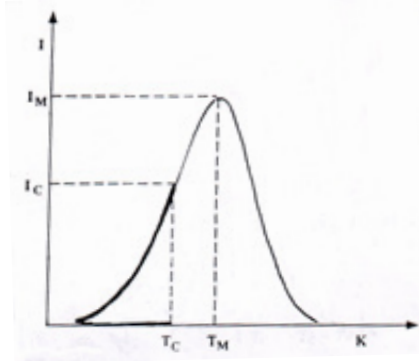
Clearly then, a plot of $\ln(I)$ versus $1/T$ over this initial rise region, results in a straight line of slope $(-E/k)$, so the activation energy is easily found without any knowledge of the frequency factor s . An example of the initial rise plot is given in Fig 2.

Fig.2. *Example of Initial-rise plot*
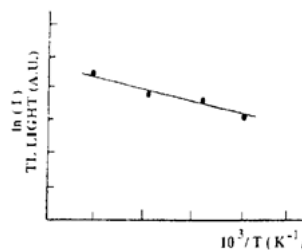
Haake (1957) has analysed the method and concluded that the straight line on a $\ln(I)$ versus $1/T$ plot is not the criteria to use for the applicability of the technique .He demonstrated that up to a certain critical value of the temperature T_c , this assumptions remains valid and T_c is considerably less than peak temperature T_M . Kivits and Hagebuek (1977) demonstrated   that the temperature T_c must not correspond to an intensity which is more than approximately 10-15% of maximum intensity. Nevertheless, in some special cases it was shown by Braunlich (1967) that the equation cannot be used even in this region. The obtained values for E are smaller than the real ones unless a condition of the form $Rh(T_0)(2/z-1) \leq f(T_0)$ is fulfilled. Here R is the retrapping factor, z the filling ratio of the traps at the temperature T_0 , f the

concentration of unoccupied recombination centers and h the density of trapped electrons. So for proper application of the method, adequate information at least on the parameters R and $h(T_0)/f(T_0)$ is needed.

Aramu et al. (1966) applied the initial rise method taking into account the temperature dependence of frequency factor s of type $s = s_0 T^\alpha$ with $-2 \le \alpha \le 2$. In this case,

$$I \propto T^\alpha \exp\left(-\frac{E}{kT}\right)$$

Denoting activation energy obtained from original initial rise method as E_{ir} , he obtained activation energy E from the above equation as $E = E_{ir} - \alpha kT$. This means the need to correct E by a few percent irrespective of the kinetics (Gartia et al, 1992).

An alternative graphical method was proposed by Ilich(1979). Taking a point on initial rise side of an isolated TL peak, a tangent is drawn in the point $N \equiv (T_c, I_c)$ (Fig.3) and slope is calculated. It is assumed that $I(T)$ has the form (initial rise region)

$$I(T) = c \exp\left(-\frac{E}{kT}\right) \text{ (c is a constant)}$$

$$\frac{dI}{dT} = c\frac{E}{kT^2}\exp\left(-\frac{E}{kT}\right) = I\frac{E}{kT^2}$$

Fig.3. *Example of Tangent method proposed by Ilich*
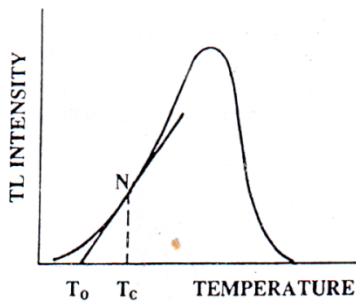
So, slope of the tangent is given by ,

$$\left.\frac{dI}{dT}\right|_{T=T_C} = I_c \frac{E}{kT_c^2} \text{ (shown in Fig.3)}$$

$$I - I_c = \frac{I_c E}{kT_c^2}(T - T_c)$$

To find the point $M(T_0, 0)$:

So, $E = k\dfrac{T_c^2}{T_c - T}$ The maximum error in this procedure is assessed from

$$\ln E = \ln k + 2\ln T_c - \ln(T_c - T_0)$$

$$\frac{\Delta E}{E} = 2\frac{\Delta T_c}{T_c} + \frac{\Delta T_c}{T_c - T_0} + \frac{\Delta T}{T_c - T_0}$$

If $\Delta T_c = \Delta T_0 = \Delta T$, then maximum possible error is ,

$$\left|\frac{\Delta E}{E}\right|_{max} = 2\Delta T\left|\frac{1}{T_c} + \frac{1}{T_c - T}\right|$$

Selecting a large number of points (T_c, I_c) and processing statistically, reliability of the results can be improved.

Halperin and Braner(1960) in their investigation of TL in alkali halides suggested an improvement of this method. Using the general order equation, $I = sn^b \exp\left(-\frac{E}{kT}\right)$, one can plot the $\ln\left(\frac{I}{n^b}\right)$ vs. $1/T$ and get the slope equal to (-E/k). The straight line will only emerge when the correct, known value of b is inserted. When b is unknown, several lines are drawn with various values of b and the best straight line is chosen. The value of n is estimated by the area of the glow peak from a given point T_0 in the initial rise region to the end of the peak as shown in Fig.4. The value of n is calculated by using

$$n = \int_{t_0}^{t_f} I dt = \frac{1}{\beta}\int_{T_0}^{T_f} I dt$$

Fig.4. *Calculation of n from a glow-curve*
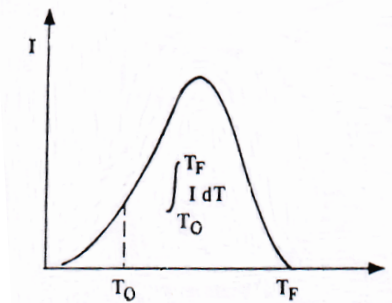
Since initial rise method is based on the approximation of the integral , it leads to a systematic error so that the computed value of trap depth becomes lower than its actual value. Christidoulides(1985) has shown that in the determination of activation energy in thermoluminescence by the initial rise method, there is always an involvement of systematic error which is significant if high levels of signal are used. He derived an expression which may be used to correct the error involved. In trying to do so has assumed that the peaks obey first order kinetics. However, the kinetics of a TL peak need not be always first order kinetics. Singh et al (1988) suggested a prescription to correct this error. They assumed general order case where the order of kinetics lies in the range 0.7 to 2.5 (covering all the practical cases known) which includes the famous first-order (b=1) and second order (b=2) cases. The applicability of these expressions have also been tested on some experimental peaks of Orthoclase(KAlSi$_{3O8)}$. Singh et al (1990) in a further work has shown that IR method can be used irrespective of order of kinetics.

Mandowski and Swiatek (1996) derived two new generalized initial rise equations which can be successfully applied to the whole TL peak with an error less than 0.1%. They checked the validity of their equations by comparing them with exact solutions of classical Garlick –Gibson initial rise equations. A slight difference between these two solutions was observed only for extremely low

values of recombination coefficient within small initial region of the TL peak. This method was found to be accurate even in the case when the initial part of the peak giving the false straight line.

So in all these approaches, the application of initial rise method has so far been limited to finding the activation energy. Therefore one has to resort to other methods of glow curve analysis to evaluate b and s

Rawat et al (2009) suggested a method those parameters from Arrhenious plots of the initial rise part of the TL glow curve. They

$$\ln I(T) = \ln Cs'n^b - E/kT$$

rewritten the general order eqn. of May and Patridge(1964)
$$I(T) = \ln Cs'n^b \exp(-E/kT) \qquad \text{as}$$

in the initial part where $n = n_0$ (initial concentration of trapped electrons)applies .The first term in the R.H.S is intercept on the $\ln I(T)$ vs. $1/T$ straight line.

Writing $I_2 = \ln Cs'n_0^b$
$I_2 - I = \ln X^b$
and increasing the dose of the sample by X, one can write,

$$b = \frac{I_2 - I_1}{\ln X}$$

$I_2 = \ln Cs'(Xn_0)^b$
So,
Thus ,

The intercepts being measurable at two doses differing by a factor X, the b values may be readily found. Here it is assumed that the traps fill linearly with dose and the total TL intensity also grows linearly with trap occupancy.

$s' = Anti\log[I - \ln Cn_0 - (b-1)\ln n_0]$ Again rearranging the original May and
$s = Anti\log[I - \ln A - (b-1)\ln(n_0/N)]$
Patridge equation in the form
$I_2 = \ln s' + \ln Cn_0 + \ln n_0^{b-1}$, one can write
and

Where , $A = Cn_0$ the area under TL peak and N the total number of traps.

Rawat et al (2009) checked the validity of these equations with a number of numerically generated curves using a wide range of input parameters and using Runge-Kutta second order technique. They also extended their work for experimental glow curves of CaSO4:Dy The experimentally calculated TL parameters using their proposed technique was satisfactory and matched with the literature. Jose et al (2011) reported the kinetic parameters of Tm doped LiCaBO3 phosphor synthesized by high temperature solid state diffusion technique following Rawat et al (2009). Their results were in good agreement with those calculated by various heating rate method.

The essence of the technique lies in the fact that all the parameters can be determined independently. The uncertainty and error associated with one parameter does not propagate into the determination of another. Moreover the expressions are applicable to the glow peaks of any order of kinetics, irrespective of whether the said peaks are of first, second or general order.

Some theoretical (Braunlich,1967; Aramu *et al,* 1966) as well as experimental (Haake,1957) reasons limit the use of the initial rise method. Braunlich (1967) showed that if a trap is filled to saturation, too small values of activation energy is found. Initial rise method suffers the difficulty due to thermal quenching as extensively discussed by Wintle (1975). According to her, due to the presence of thermal quenching, the value of activation energy will be lower than the actual value by an amount 'W' which is the energy depth characterizing the non-radiative process. Complete isolation of the peaks which is a primary requisite of this method is the principle difficulty with this problem. It is pointed out that, initial rise method can only be used when the glow peak is well-defined and clearly separated from other peaks. To improve the initial rise method, when a TL peak is composed by a superposition of two or more peaks, several methods of peak separation has been devised. Among them, the most popular method is so-called 'thermal cleaning' technique described by Nicholas and Woods(1964). A more accurate technique , called fractional glow (FG) has been introduced by Gobrecth and Hofmann(1966).

2. Conclusion

Initial rise method can be used to determine activation energy in thermoluminescence. Even if frequency factor is temperature dependent, still the method can be used leading to an error of about 5-10% in the determination of activation energy.

Initial rise method can not only be used in TL. It can easily be applied under certain conditions to a number of related phenomenon(Chen & McKeever, 1997) such as thermally stimulated conductivity(TSC), thermally stimulated electron emission (TSEE), ionic thermocurrent(ITC), derivative thermogravimetry (DG), differential thermal analysis (DTA), thermal desorption. Although highly sophisticated and rigorous methods have been developed for the purpose of analysis of TL glow curve, the relevance of classical methods such as Initial rise method will not be lost. There is ample scope to improve its acceptability and make it more sophisticated.

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