CHAPTER VI

THERMOLUMINESCENCE
6.1 Introduction

Thermoluminescence is the phenomenon of luminescent emission after removal of the excitation under conditions of increasing temperature or thermoluminescence may also be defined as thermally stimulated release (in the form of optical radiation) of energy stored in a material by previous excitation. Thermoluminescence and incandescence may be distinguished since luminescence usually lies in a spectral region where the material is non-absorbing while the incandescence emissivity is strongest where absorptivity of the material is the maximum. The process of thermoluminescence is essentially the same as that of phosphorescence, thermal energy being responsible for liberation of trapped electrons or holes in both cases. The only difference is that phosphorescence occurs at a certain fixed temperature while in thermoluminescence (TL) the temperature changes.

Thermoluminescence is a convenient tool for studying traps in crystals. It involves radiative recombination of thermally released electrons or holes from their traps with the charges of opposite sign at the recombination centres.

In thermoluminescence the phosphor is usually excited by exciting radiations such as U.V., X-rays or ionising particles at a fixed low temperature to fill all empty traps and then it is allowed to decay for a sufficient time so that shallower traps are
emptied. Now the phosphor is heated at a constant rate in the dark. Charge carriers in the filled traps get thermal energy and the "frozen in" luminescence is released. The plot of luminescence intensity versus temperature is known as "glow curve" which shows a peak for each group of traps. Hence TL is an efficient technique to get information about traps and to understand the exact nature of trapping states. 2-5

Since the thermoluminescence phenomenon is due to the presence of different intrinsic defects and impurity centres, it gives information about defect structure and damage processes in different materials provides the identity of the centres that cause TL peaks, can be established. 5

Thermoluminescence is affected by a number of factors such as impurities (activator, poison, sensitizer), thermal annealing, irradiation dose etc. 1 The colour of TL is found to be very sensitive to the presence of impurities. 7 It has also been shown that fast cooled samples (during preparation) give more efficient TL radiation than the slow cooled samples because of the larger number of defects frozen-in. Thermoluminescence has very useful applications in the analysis and identification of minerals, dosimetry, radiation damage, stratigraphic correlation of rocks, geological age determination and temperature of intrusions. 10 Thermoluminescence can be applied after proper calibration in the field of forensic science, 11 dating of potteries 12 and thermography 13 etc.
5.2 Theoretical aspect of thermoluminescence:

The phenomenon of thermoluminescence (TL) was known for nearly three centuries but the basic mathematical understanding was first provided by Randall and Wilkins only in 1945. The last two decades have witnessed a rapid development in this field. 1

(a) Randall and Wilkins theory — The basic theory of TL given by Randall and Wilkins 14 provided the simplest mathematical representation for the luminescence glow peaks without any overlapping. The basic assumptions they made were that once an electron escapes from a trap there is no significant probability for it to get retrapped (i.e., monomolecular mechanism) and that the luminescence intensity at any temperature is directly proportional to rate at which the detrapping occurs.

During heating, if $n$ is the concentration of filled traps at any instant $t$, the intensity $I$ is given by the equation:

$$ I \propto \frac{dn}{dt} $$

or

$$ I = C \frac{dn}{dt} $$  \hspace{1cm} (5.1)

$$ \frac{dn}{dt} = -nSe\left[-\frac{E}{kT}\right] $$  \hspace{1cm} (5.2)

or

$$ I = -CnSe\left[-\frac{E}{kT}\right] $$  \hspace{1cm} (5.3)
where $C$ is a constant of proportionality and is considered to be unity, $S$ is called the escape frequency (having dimensions of sec$^{-1}$), $T$ is the absolute temperature and $k$ is the Boltzmann constant.

From equation (5.2):

$$\frac{dn}{n} = - S e^{\frac{-E}{kT}} \, dt \quad (6.4)$$

If $\frac{dT}{dt} = \beta$ be the uniform heating rate, equation (6.4) can be written as:

$$\frac{dn}{n} = - \frac{S}{\beta} e^{\frac{-E}{kT}} \, dT$$

On integrating, we have:

$$n = n_0 \exp \left[ - \int_{T_0}^{T} \frac{S}{\beta} e^{\frac{-E}{kT}} \, dT \right] \quad (6.5)$$

from equation (5.3) and (6.5):

$$I = n_0 S \exp \left(\frac{-E}{kT}\right) \cdot \exp \left[ - \int_{T_0}^{T} \frac{S}{\beta} e^{\frac{-E}{kT}} \, dT \right] \quad (6.6)$$

$T = T_0 + \beta t$, where $T_0$ is the initial temperature.

By differentiating and equating to zero one finds the condition for maximum i.e.,

$$\frac{\beta E}{kT_m^2} = S \exp \left( - \frac{E}{kT_m} \right) \quad (5.7)$$

where $T_m$ is the temperature at maximum of the glow peak. Hence if $S$ is known, this equation should serve as a transcendental
equation to be solved numerically for $E$.

(b) Garlick and Gibson's theory — The above theory given by Randall and Wilkins is based on the assumption that retrapping is a negligible process in the phosphor. Garlick and Gibson\textsuperscript{15} however modified the theory arguing that an electron escaping from a trap has the same probability of being trapped as it has of recombining with an empty luminescence centre.

Let $N$ be the total number of electron traps, out of which $n$ are filled by electrons at any instant. Then there will be $(N - n)$ empty traps and $n$ empty luminescence centres previously vacated by electrons. The probability that an escaping electron will recombine with an empty luminescence centre and not be retrapped is given by:

$$\frac{n}{(N-n) + n} = \frac{n}{N} \quad (6.8)$$

and the luminescence intensity at any instant (i.e., the rate of escape of electrons from the trap) will be given by:

$$I = -\frac{dn}{dt} = \left(\frac{n^2}{N}\right) S \exp \left(-\frac{E}{kT}\right) \quad (6.9)$$

This case is usually referred to as "second order kinetics". According to Garlick and Gibson, the second order kinetics apply when retrapping and recombination probabilities are equal. The
solution of equation (6.9) is:

\[ I = \frac{n_0^2 S \exp \left( -\frac{E}{kT} \right)}{N \left[ 1 + \frac{n_0}{N} \int_{T_0}^{T} \frac{S}{\beta} \exp \left( -\frac{E}{kT} \right) dT \right]^2} \tag{6.10} \]

where \( \beta \) is the uniform rate of heating and \( n_0 \) is the value of \( n \) at \( t = 0 \). The term in brackets in equation (6.10) as well as the right hand exponential term in equation (6.9) varies only slightly when \( T \ll T_m \). Therefore in this region,

\[ I \propto \exp \left( -\frac{E}{kT} \right) \tag{6.11} \]

This provides a simple means for calculating the activation energy from the slope of a plot of \( \log I \) versus \( (1/T) \) in the initial rise region. 15,16 The initial rise method is considered to be valid for intermediate order kinetics as well. 17 However some experimental 18 as well as theoretical 19,20 reasons limit its use.

5.3 Methods for evaluation of trap depth \( E \):

There are a number of methods developed for calculating trap depth \( E \), from glow curves. Some of them depend on the peak temperature and others on the shape of the glow curve.

These methods can be classified into two main groups.

(A) Methods independent of the shape of the glow curve (i.e., those, which depend on \( T_m \) mainly).
(8) Shape methods (i.e., those which depend on the shape of the glow curve).

A **Methods independent of the shape of the glow curve.**

I **Methods sensitive to recombination kinetics.**

(a) **Randall and Wilkins' method** - The expression (5.5) represents the glow curve for only a single trap depth. The glow curves for most phosphors would have to be calculated by integration over the distribution of trap depths. However, Randall and Wilkins have shown that the mean life time of the trapped electrons is little different from one second at the temperature of maximum glow, \( T_m \). Hence on the basis of equation (5.7) one can easily write:

\[
E = K T_m \left[ 1 + f \left( S, \beta \right) \right] \log_e S
\]

(5.12)

where

\[
f \left( S, \beta \right) = \frac{\log \left( K T_m^2 / \beta E \right)}{\log S}
\]

is a small correction factor of the order of 0.1 and may be neglected. Hence equation (5.12) reduces to:

\[
E = K T_m \log_e S
\]

or

\[
E = 2.303 K T_m \log_{10} S
\]

(5.13)

The value of \( S \) is different for different phosphors as reported by many workers. 21,22
(b) Urbach formula: Urbach found empirically that a reasonable estimate for trap depth $E$ in electron volts is given by:

$$ E = \frac{T_m}{500} $$  \hspace{1cm} (6.14)

which gives the right order of values for heating rates at about $1^\circ K/\text{sec}$.

(c) Curie formula: On the basis of equation (6.7) Curie has given the following formula for trap depth.

$$ E = \frac{T_m (\Theta K) - T_o (\beta/s)}{\Theta (\beta/s)} $$  \hspace{1cm} (6.15)

where $T_o$ and $\Theta$ are constants dependent on parameter $\beta/s$. The values of these constants for a particular value of $\beta/s$ can be obtained graphically with the help of table provided by Curie.

(d) Booth and Bohun's method: Booth and Bohun suggested independently a method for evaluation of trap depth $E$, by using different heating rates $\beta_1$ and $\beta_2$.

They obtained:

$$ E = \frac{K T_m}{T_m - T_{m2}} \times \log \frac{\beta_1 T_{m2}^2}{\beta_2 T_m^2} $$  \hspace{1cm} (6.15)

hence $S$ is eliminated.
The value of $S$ can be obtained by the relation,

$$\log \frac{K_S}{E} = \frac{T_m^2 \log (T_m^2 / \beta) - T_m \log (T_m^2 / \beta)}{T_m - T_m^2}$$

(6.17)

Another way to find $E$ is to use several heating rates and plotting $\log \left( \frac{T_m^2}{\beta} \right)$ versus $1/T_m$ which should yield a straight line with slope $E/K$.

(e) Isothermal decay method - In this method the sample is quickly heated to a specific temperature (after initial excitation) and phosphorescence decay is measured by maintaining the sample isothermally at this temperature. The method being isothermal, it has the advantage that such difficulties as arising from overlapping peaks and change in quantum efficiency or the emission spectra occurring under the non-isothermal conditions, are avoided. The decay curve obtained can be analysed and it has been shown that for first order kinetics:

$$I(T) = n_0 S \exp \left( -E/kT \right) \exp \left[ -St \exp \left( -E/kT \right) \right]$$

(4.18)

t being the time.

$$\log_e I(T) = \left[ \log n_0 S - E/kT \right] - St \exp \left( -E/kT \right)$$

(4.19)

Hence the slope $m = \frac{d}{dt} \log I(T)$ versus $t$ curve is given by:

$$m = S \exp \left( -E/kT \right)$$

(4.20)

taking $m_1$ and $m_2$ i.e., the slopes of the curves at two different
temperatures one can get:

$$\log \frac{m_1}{m_2} = \frac{E}{K} \left( \frac{1}{T_1} - \frac{1}{T_2} \right)$$  \hspace{1cm} (6.21)

which can be used to determine the activation energy $E$. The frequency factor $S$ may be found by using equation (6.20).

(f) **Inflection point method** - This method was proposed by Land. According to him, the second derivative of TL intensity with respect to temperature is zero at the inflection points. The second derivative i.e. $\frac{d^2I}{dT^2}$ of Randall and Wilkins TL intensity relation (5.5) was taken and equated to zero. Positive real roots of this equation provide $T_1$ and equation for trap depth comes out to be:

$$E = \frac{K T_m T_1}{(T_1 - T_m)} \log \frac{A}{(T_1 / T_m)^2}$$  \hspace{1cm} (6.22)

where $A = 0.77$ and $2.55$ respectively for $T_1 < T_m$ and $T_1 > T_m$ for first order kinetics and $A = 0.24$ and $3.43$ respectively for $T_1 < T_m$ and $T_1 > T_m$ for second order kinetics. Thus by measuring $T_1$ and $T_m$, $E$ can be determined.

The frequency factor is given by:

$$S = \beta \left[ \frac{E}{kT} \exp \left( \frac{-E}{kT} \right) \right]$$  \hspace{1cm} (6.23)

This method has the advantage of fine resolution even in the case of close lying peaks and $E$ and $S$ values can be obtained for all
peaks from a single glow curve.

II Methods independent of recombination kinetics

(a) **Hoogenstraaten method** - Using equation (6.7), Hoogenstraaten 15 has shown that peak temperature $T_m$ is related to $E$ by the equation:

$$\log \left( -\frac{T_m^2}{\beta} \right) = \frac{E}{K T_m} + \log_e \frac{E}{SK} \quad (6.24)$$

Thus the plot between $\log_e \frac{T_m^2}{\beta}$ versus $1/T_m$ is linear with a slope equal to $E/K$ and making an intercept of $\log_e \frac{SK}{E}$. Thus both $E$ and $S$ can be determined.

(b) **Initial rise method** - This method suggested by Garlick and Gibson assumes the following :-

(i) In the initial rising range of temperatures i.e., $T \ll T_m$ the rate of change of trapped carrier population is negligible and hence the intensity in the initial part of the curve is strictly proportional to $\exp (-E/kT)$:

$$\text{i.e., } I \propto \exp (-E/kT)$$

(ii) The frequency factor $S$ remains constant i.e., it is independent of temperature.

(iii) There is no overlap of peaks belonging to different trapping levels.

$$I = F \exp (-E/kT) \quad (6.25)$$

$F$ being a constant in the initial part of the curve.
\[ \text{Hence } \log_e I = - \frac{E}{kT} + \text{constant} \quad (5.25) \]

A plot of \( \log I \) versus \( 1/T \) should give a straight line, the slope of which yields the value of \( E \).

(c) **Area measurement methods** - These methods essentially stem from the fact that the filled trap density at any temperature \( T \) is proportional to the remaining area of the glow curve, \( S(T) \).

(i) **Method due to Muntoni et al.** - Muntoni et al. \(^{32}\) proposed a method for trap depth calculation by considering the following equation which is based on the equation proposed by Romanovskii \(^{33}\) and Lushchik \(^{34}\) i.e.,

\[ I \propto \frac{dm}{dt} = A m^\alpha e^{-E/kT} \quad (5.27) \]

where \( m \) is the density of recombination centres, \( A \) is a proportionality constant and \( \alpha \) is a suitable numerical parameter representing the order of kinetics.

For uniform heating rate \( \beta \) the above equation can be written as:

\[ I = a \beta \frac{dm}{dt} \quad (5.28) \]

where \( a \) is a factor depending on the efficiency of the light detecting unit. On integrating, the above equation reduces to:

\[ m(T) = \frac{S(T)}{a \beta} \quad (5.29) \]
where $S(T)$ is the integrated area of the curve in the interval from $T$ to $T_0$; $T_0$ being the temperature corresponding to the end of the glow curve. The above equation may be written as:

$$\log \frac{I(T)}{[S(T)]^\alpha} = \left( -\frac{E}{kT} \right) + C \quad (5.36)$$

where $I(T)$ is the TL intensity at temperature $T$ and $C = \log \left( A_a (1+\alpha) a^{-\alpha} \right)$. Value of $\alpha$ corresponding to linear plot of $\log \frac{I(T)}{[S(T)]^\alpha}$ versus $1/T$ represents the order of kinetics involved and the slope of the straight line thus obtained gives the value of the trap depth.

(ii) **Method due to Maxia et al.** Maxia et al. 35 proposed another method involving area measurement for calculation of trap depth. Starting from kinetic equation (5.3) they obtained the following relation:

$$\log \left[ \frac{I(T) \cos \Theta + \sin \Theta \cdot S(T)}{S^2(T) + \Delta ST} \right] = -\frac{E}{kT} + \mu \quad (5.31)$$

Or $$\gamma = \frac{E}{kT} + \mu \quad (5.32)$$

where $\gamma$ is written for term on left hand side of equation (5.31) and $\nu = 1/T$, $\Theta$ is a function of area of the glow curve and the probability factors for recombination and retrapping which determine the linear behaviour of $\nu$ and $\gamma$. All quantities on the left hand side of the equation can be determined from the TL spectrum, except $\Theta$. 
The correlation coefficient

\[ \rho = \frac{\text{Cov}(x, y)}{\sqrt{\text{Var}(x) \cdot \text{Var}(y)}} \] (5.33)

can be numerically computed as a function of \( \theta \) and is conditioned for \( \rho \) or \( \rho^2 \) attaining unity. From this the activation energy is given by:

\[ E = -K \frac{\text{Cov}(x, y)}{\text{Var}(x)} = -K \frac{\text{Cov}(x, y)}{\text{Var}(y)} \] (5.34)

Aramu and Maxia proposed a simpler procedure which is an extension of the initial rise method but also involving area measurement. The conventional Arrehenius diagram is modified with each value of \( I(T) \) normalised to the total area of saturated glow peak i.e., \( \log \left( \frac{I}{S_0} \right) \) is plotted against \( 1/T \) for the full glow peak where \( S_0 \) is the area of the saturated glow peak. Such a normalised glow peak has a straight line portion for larger values of \( 1/T \) as in the initial rise method and is governed by:

\[ \log \left( \frac{I}{S_0} \right) = \left( -\frac{E}{K} \right) \cdot \left( \frac{1}{T} \right) + \eta \] (5.35)

Hence slope of this straight line provides \( \frac{E}{K} \) and the value of frequency factor is governed by:

\[ S = \beta \cdot e^\eta \] (5.35)
B Shape methods

There are several equations developed with determination of trap depths which depend on $T_1$, $T_2$ and $T_m$ i.e., first and second half intensity temperatures and temperature of the maximum of the glow peak respectively. The formulae for finding the energies by these methods usually contain one of the following factors: (a) $\tau = T_m - T_1$, the half width on the low temperature side of the peak, (b) $\delta = T_2 - T_m$, the half width towards the fall off of the glow peak and (c) $W = T_2 - T_1$, the total half width of the glow peak.

(a) Grosswiener's formula

Grosswiener derived the following formula for the case of first order kinetics using only the ascending part of the glow peak.

\[
\text{Trap depth } E = \frac{1.51 k T_m T_1}{\tau} \quad (6.37)
\]

which he claims to be accurate to better than \( \pm 3\% \) provided that

\[
\frac{S}{\beta} > 10^7 \text{ deg}^{-1} \quad \text{and} \quad \frac{E}{kT_m} > 20.
\]

Substituting this value of $E$ in equation (6.7) one can get:

\[
S = 1.51 \left( \frac{\beta T_1}{T_m} \right) \exp \left( -\frac{1.51 T_1}{\tau} \right) \quad (6.39)
\]

Dussel and Bube showed that Grosswiener's method for $E$ is, out by about $7\%$ and gave other similar formulae for $E$.

Chen corrected Grosswiener's formula as follows:
\[ E_{GC} = \frac{1.41 \ k \ T_m \ T_1}{T} \]  
(For 1st order kinetics)

and,
\[ \delta_{GC} = \frac{1.69 \ k \ T_m \ T_1}{T} \]  
(For 2nd order kinetics)

Results are now within ±1.5% throughout the broad E and S ranges.

(b) Lushchik's formula - Lushchik \(^{34}\) assumed the area of the half peak towards the fall off portion of the glow curve to be equal to the area of the triangle having the same height and half width, and obtained the following formulae for trap depth.

\[ E = \frac{k \ T_m^2}{\delta} \]  
(For 1st order kinetics)

and
\[ E = \frac{2 \ k \ T_m^2}{\delta} \]  
(For 2nd order kinetics)

Chen \(^{39,40}\) modified these relations as follows:

\[ E = \frac{0.375 \ k \ T_m^2}{\delta} \]  
(For 1st order kinetics)

and
\[ E = 1.70 \left( \frac{k \ T_m^2}{\delta} \right) - 2 \ k \ T_m \]  
(For 2nd order kinetics)
(c) **Halperin and Braner's method** — In this method the symmetry of the glow peak about its maximum is taken into account. Halperin and Braner[17] considered the thermoluminescence emission as mainly due to two kinds of recombination processes:

(I) The trapped electron is raised thermally from the ground state of the trap to an excited state below the conduction band from which it may recombine with a trapped hole by tunneling process.

(II) It is raised directly to the conduction band, where it is free to move and may finally recombine with a trapped hole.

Halperin and Braner obtained the following general equations for evaluating the activation energy.

(i) For carriers raised into a level in the forbidden gap.

\[ E = q \frac{kT_m^2}{\varepsilon} \]  \hspace{1cm} (5.45)

(ii) For carriers raised directly to the conduction band.

\[ E = q \frac{kT_m^2}{\varepsilon} (1 - \Delta) \]  \hspace{1cm} (5.45)

where \( \Delta = \frac{2kT_m}{E} \) is a correction factor, usually of the order of 0.1.

The value of \( q \) depends on the order of process.

For first order process they[17,41] found it to be:

\[ q_1 = 1.72 \mu g \left( \frac{1 - 1.59\Delta}{1 - \mu g} \right) \]
and for second order process:

\[ q_2 = 2 \mu g \left( \frac{1 - 2\Delta}{1 - \mu g} \right) \]

where \( \mu g = \frac{n_m}{n_0} \), \( n_0 \) being the initial concentration of trapped carriers and \( n_m \) the concentration of trapped carriers at \( T_m \).

For evaluating order of the process, Halperin et al. \( ^{41} \) used the following values of \( \mu g \),

\[ \mu g \approx \left( \frac{1 + \Delta}{e} \right) \quad \text{For 1st order process} \]
\[ (e = 2.718 \ldots) \]

and \( \mu g \approx \left( \frac{1 + \Delta}{2} \right) \quad \text{For 2nd order process} \).

\( \mu g \) is also taken to be equal to \( \mu_g \) (the geometrical shape factor) as an approximation.

They \( ^{17} \) have also shown that a method based on \( \tau \) is expected to be more accurate in many cases. By assuming \( \mu g = \mu_g \), they obtained the following equation for first order kinetics when excitation is into the band, i.e.,

\[ E = 1.72 \left( \frac{kT_m}{\tau} \right)^2 (1 - 1.58\Delta) \quad (5.47) \]  

and \[ E = \frac{2kT_m}{\tau} (1 - 3\Delta) \quad \ldots \quad (5.47) \]

\ldots for second order kinetics.
For activation energy calculation, \( \Delta \) is assumed to be zero first and \( E \) is found. This calculated value of \( E \) is used for determination of \( \Delta \) and then \( E \) is corrected.

Halperin and Brener's formulae were usually found to be too high by 10\% or more. Chen \(^{39}\) modified the formulae (5.45) and found them to be:

\[
E = \frac{1.52 k Tm^2}{C} - 1.58 (2 k Tm) \tag{5.48}
\]

(for 1st order kinetics)

and

\[
E = 1.813 \left( \frac{k Tm^2}{C} \right) - 2 (2 k Tm) \tag{5.49}
\]

(for 2nd order kinetics)

(d) Keating's formula

Following Lax \(^{42}\) and Bemski \(^{43}\), \(^{44}\) Keating introduced the possibility of temperature dependent frequency factors \( S = S^a T^a \) where \(-2 \leq a \leq 2\). For all values of \( a \), Keating gave the following formula for first order peaks, i.e.,

\[
\frac{k Tm}{E} = (1.2 \sqrt{1 - 0.54}) \frac{W}{Tm} + 0.0055 - \left[ \frac{1}{2} \left( \frac{\sqrt{\gamma} - 0.75}{0.75} \right) \right]^2 \tag{5.90}
\]

where \( \sqrt{\gamma} = \frac{\delta}{C} \). The formula is reported to hold true for \( 0.75 < \gamma < 0.90 \) and \( 10 < \frac{E}{k Tm} < 35 \).
(e) Chen's formulae - Chen derived formulae for calculating glow parameters by the use of half width $W$ and the maximum temperature for first and second order peaks. Some of them are given below.

For first order kinetics:

$$E_W = 2kT_m \left( \frac{1.25 T_m}{W} - 1 \right) \quad (5.51)$$

By dropping unity in the parenthesis and reducing the value of the other constants for compensation, quite a good approximation of (5.51) is given by:

$$E_Q = \frac{2.29kT_m^2}{W} \quad (5.52)$$

For second order kinetics:

$$E_W = 2kT_m \left( \frac{1.755 T_m}{W} - 1 \right) \quad (5.53)$$

Here Chen considered frequency factor $S$ to be independent of $T$ and shape factor $M_T \approx 0.42$ and 0.52 for first and second order kinetics respectively.

Using the value of $E_Q$ obtained from (5.48) or (5.49) as the case may be, the total half width $W = (T_2 - T_1)$ can be calculated from Chen's equation (5.52) or (5.53).

Also one can directly obtain the value of $W$ by insertion of (5.48) in (5.52) or equation (5.49) in (5.53) i.e.,

$$W = \frac{1.145 T_m}{0.75 \left( \frac{T_m}{\tau} \right) - 1.58} \quad (5.54)$$

(for first order kinetics)
and \[ W = \frac{2 \times 1.735 \times T_m}{1.813 \left( \frac{T_m}{T} \right) - 2} \] (for second order kinetics).

Hence using this value of \( W \) one can easily find \( \xi = (W - T) \).

(f) Chen's formulae for activation energy for general order kinetics.

These are the formulae which require no, a-priori assumption as to the order of kinetics. These are:

\[ E_T = \left[ 1.51 + 3.0 \left( \mu g' - 0.42 \right) \right] \frac{k T_m^2}{T} \]
\[ - \left[ 1.58 + 4.2 \left( \mu g' - 0.42 \right) \right] \times 2 k T_m \quad (5.55) \]

\[ E_\xi = \left[ 0.975 + 7.3 \left( \mu g' - 0.42 \right) \right] \times \frac{k T_m^2}{\xi} \quad (5.57) \]

\[ E_W = \left[ 2.52 + 10.2 \left( \mu g' - 0.42 \right) \right] \frac{k T_m^2}{W} - 2 k T_m \quad (5.59) \]

where \( \mu g' = \frac{\xi}{W} \) is the geometrical shape factor.

5.4 Experimental methods:

The method of measuring TL glow curves is the same as that of phosphorescence decay measurements, except for an additional provision for the heating of the phosphor at a uniform rate and necessary arrangement for thermal insulation.
The heating rate is an important parameter in thermoluminescence. Slow heating rate facilitates better resolution \(^{21,45}\) while high heating rate insures a sharp maximum of glow curve peaks which makes it convenient to determine the peak value. \(^{14,15}\)

Several techniques have been developed for heating the samples such as electric resistance heating, hot gas jet heating (mostly hot \(N_2\) gas), magnetic induction heating and infra-red heating. The electric resistance heating which employs a Kanthal alloy wire (or strip) is the simplest and most widely used method. The temperature of the sample under study is measured with a thermocouple.

Randall and Wilkins \(^{14}\) spread a thin layer of phosphor on the glycerol smeared surface of a copper box. A copper-constantan thermocouple was soldered on the surface of the box and liquid air was used to obtain low temperature. The phosphor was excited with a mercury arc and the glow intensity was recorded with a P.M. tube, galvanometer and recorder arrangement. Garlick \(^{47}\) improved this arrangement by putting a replaceable heater inside the copper box so as to heat the phosphor at 5 K/sec.

Shionoya et al. \(^{49}\) made the arrangement for temperature variation from 77 K to 153 K. A thin layer of phosphor was deposited on a plate attached to a copper rod. The lower half of the rod was mounted in a dewar flask containing liquid nitrogen.
This part of the copper rod was surrounded by a nichrome wire to heat up the sample. The output of the detector after proper amplification was recorded by a Sanborn recorder. A constant heating rate of 0.25 °K/sec was obtained by a cam type programme controller.

Sanzelle and coworkers 49 have designed an apparatus for measurement of TL of various phosphors in the range between 77 K and 773 K.

Bhasin 8,50 used an experimental set up which consists of a linear temperature programmer arranged for a heating rate of 10 to 100 K/min, heating chambers with provision to control the atmosphere, a P.M. tube with cooling arrangement to reduce the dark current, a double pan insulating window to avoid frosting, a high input impedance DC amplifier and a null balancing potentiometric recorder.

Recently Kaul 51 used Encardio-Rite TLD recorder system having a provision to accommodate different P.M. tubes. The temperature programmer attached with it can heat the sample from 0.5 K/sec to 90 K/sec.

Other workers 5,52-54 have used different kinds of apparatus for TL recording depending on the source of excitation, conditions and range of temperature measurements.
5.9 Present method:

A Experimental arrangement.

The assembly used and its alignment for the present TL study was the same as that described in Chapter IV (Emission). The phosphor holder cavity was in contact with the Kanthol strip heater which could be heated by applying stabilized voltage through a variac. Hence a constant alternating current is supplied to the heater so as to heat up the phosphor at a constant rate. Phosphor pressed in the cavity was excited by X-rays. The light emitted by the phosphor was received by a (IP21) photomultiplier tube and recorded by a Polyflex galvanometer (type PL 50). Stabilized power was supplied to the P.M. tube by a (900V) power supply unit. A mark on the cylinder and disc was made to keep the sample holder in the same position throughout the experiment. A water filter was used between the phosphor and the detector to avoid the effect of thermal radiations.

B Measurement of Phosphor temperature.

In order to find out the temperature of the phosphor at any instant during heating the Kanthol strip heater was calibrated using a copper-constantan thermocouple. One junction of the thermocouple was kept in melting ice and the other junction was inserted in the brass sample holder. A high
sensitivity Philips microvoltmeter was connected with the thermocouple to measure the thermo e.m.f. produced by the thermocouple. Knowing the thermo e.m.f. corresponding temperatures were noted from the standard table. 55

In order to calibrate the heating element a known current of fixed value (3.5 Amp.) was supplied with the help of an AC stabilizer and variac. Thermo e.m.f. readings in millivolts on the microvoltmeter were recorded after every five seconds till 230°C. Finally the temperatures corresponding to these millivolt readings were obtained from the standard table 57 and a graph was plotted between time and temperature (Fig. 5.1). Hence the phosphor cavity temperature at any instant could be determined from the graph.

(C) Experimental procedure.

An equal amount of the phosphor was taken every time and pressed uniformly inside the phosphor cavity, mounted in the assembly and irradiated by X-rays (30kV, 10 mA) for five minutes (saturation time for excitation), then allowed to decay in the dark to a very low value of phosphorescence intensity so that shallow traps get emptied. The photomultiplier was opened. Afterwards heater current of fixed value (3.5 Amp.) was switched on and stop watch was started at the same time. The galvanometer deflection was noted as a function of time and with the help of
FIG: 6.1 - CALIBRATION CURVE (HEATER CURRENT 3.6 AMPERE).
the calibration curve corresponding temperatures were noted. Finally glow curves were plotted between temperature in K and TL intensity in arbitrary units. In the present study all phosphors were heated from room temperature to 500 K at 0.733 K/sec.

To ascertain the colour of TL the complete experimental set up described in Chapter IV (Emission) was used along with provision of keeping the phosphor at different temperatures.

The distance of the phosphor cavity from X-ray slit was kept constant throughout the present study.

6.6 Analysis of non-isolated TL glow peaks

Activation energy corresponding to any isolated glow peak can be easily calculated by any of the formulae given earlier. But a non-isolated glow peak effectively limits the accuracy of evaluation of activation energy. Hence some method of cleaning is necessary to analyse the complex glow curves.

A number of analytical methods and models have been proposed by different workers 55-59 for analysing thermal glow curves, but resulting in somewhat widely different conclusions even for the same system.

Rao 50 has proposed a simple method of analysing the glow curves, but the method does not deal with the cases where the glow peak maximum changes due to interference from the preceding peak. A modified analytical method for analysing complex TL glow curve
has been suggested by Khare et al. 51 for two cases i.e., (1) when glow peak maximum is unaffected by the neighbouring peak, (ii) when glow peak maximum is affected by the neighbouring peak. In the first case they have started from low temperature side, while in the second case from the high temperature side of the glow curve and found somewhat satisfactory results in the case of CaO phosphors, using Chen's formulae.

Some workers have proposed empirical methods for isolating TL glow peaks by proper thermal treatment 15,17,54,52-54 or by optical bleaching. 55 Before applying the method of thermal cleaning it is expected that crystal should exhibit a reproducible glow pattern after undergoing continuous heat treatments.

In the present method, thermal cleaning of the first glow peak was based on the methods followed by Hoogenstraaten, 16 Gartia 54 and Kathuria 52 because of the simplicity and reproducibility of the results within our temperature limits. The phosphor was excited by X-rays for five minutes. After its decay to negligible intensity, it was heated to 500 K at the rate of 0.733 K/sec. Hence a complex glow curve (a) was obtained.

Afterwards the same sample was again excited under similar conditions of temperature by X-rays for the same time, then heated to the temperature of the first peak, i.e., 355 K and cooled to room temperature in the dark. The sample was heated again at the same rate from room temperature to 500 K. Thus glow curve (b) is
obtained. It is seen that first glow peak is completely bleached in each case. This first glow peak is obtained by normalizing the curve (b) so as to have a close fit with the falling side of the curve (a). By subtracting curve (b) from curve (a), curve (c) is isolated.

5.7 Results

(a) Glow curves - The glow curves for the phosphors of different series are shown in Figs. 5.2 to 5.4.

No recordable TL glow was found for phosphors with host composition ZnO : MgO (10:1) and ZnO : MgO (9:1).

All phosphors having Eu activator show a complex (non-isolated) glow curve in the temperature range 300 K to 500 K. The first glow peak occurs at about 355 ± 2 K while the position of second glow peak varies regularly from 405 K to 444 K, as proportion of MgO in ZnO increases, as found on thermal cleaning of first glow peak and shown in Fig. 5.2 and 5.3.

In ZnO(1-x): MgO(x) : Eu (i.e., E-series) phosphors the intensity and intensity ratio of second glow peak to first glow peak increases as MgO proportion increases. In the case of E7 sample the intensity of both peaks is comparable hence the resultant glow curve shows a peak at about 334 K, while for E8 sample, the intensity of second glow peak is greater than that of first glow
FIG: 6.2 [A, B, C] - GLOW CURVES OF ZnO: MgO: Eu PHOSPHORS UNDER X-RAY EXCITATION.
FIG. 6.2 [D, E] - GLOW CURVES OF $\text{ZnO : MgO : Eu}^{(1-x)}(x)$ PHOSPHORS UNDER X-RAY EXCITATION.
FIG. 6.2[F] - GLOW CURVES OF ZnO:MgO:Eu PHOSPHORS UNDER (1-x) (x) X-RAY EXCITATION.
FIG: 6.2 [G] - GLOW CURVES OF ZnO : MgO : Eu PHOSPHORS UNDER X-RAY EXCITATION.
FIG: 6.2 [H] - GLOW CURVES OF ZnO : MgO : Eu \((1-x)\) \((x)\) PHOSPHORS UNDER X-RAY EXCITATION.
FIG. 6.2[1] - GLOW CURVES OF ZnO : MgO : Eu PHOSPHORS UNDER X-RAY EXCITATION.
FIG. 6.3 [A, B, C] - GLOW CURVES OF ZnO:MgO:([Eu 0.05%, Sm 0.01%] 
(1-x)) 
PHOSPHORS UNDER X-RAY EXCITATION.
FIG 6.3(D) - GLOW CURVES OF ZnO : MgO : [Eu 0.05%, Sm 0.01%] PHOSPHORS UNDER X-RAY EXCITATION.
FIG: 6.4 [A, B, C] - GLOW CURVES OF ZnO: MgO (7:3) : [Eu, Sm(x)]
(l-x) (x)
PHOSPHORS UNDER X-RAY EXCITATION.
FIG. 6.4 [D,E,F] - GLOW CURVES OF ZnO: MgO (7:3) [Eu, Sm (x)]

PHOSPHORS UNDER X-RAY EXCITATION.
peak such that the super position of the two represent a ladder like nature at about 355 K. Approximately similar results were observed with ZnO(1-x) : MgO(x) : Eu (0.05%), Sm (0.01%) - (i.e., es_x - Series ) phosphors as shown in Figs. 5.2 and 5.3.

The TL intensity ZnO(1-x) : MgO(x) : Sm phosphors is found to be very poor and unrecordable in the present study.

No appreciable increase in glow peak intensity or change in glow peak temperature is observed with initial increase in Sm concentration in ZnO : MgO (7:3) : ( Eu 0.05%, Sm_x) (i.e. X - Series ) phosphors but as the concentration of Sm approaches 0.1 mole % a slight reduction in glow peak intensity is observed ( Fig. 6.4 ).

From the nature of the descending portion of second glow peak one can suspect the presence of some other higher temperature glow peaks which may be similar to those observed by various workers 5,65 in the case of MgO phosphors.

(b) Colour of TL - The colour of TL was ascertained by the glow curves obtained at peak wavelengths of the emission spectrum. ZnO(1-x) : MgO(x) : Eu and ZnO(1-x) : MgO(x) : ( Eu 0.05%, Sm 0.01%) phosphors emit lines peaking at 593 nm and at about 511 nm. Hence to verify the colour of TL, the arrangement was made similar to that for emission spectrum
(Chapter IV). The drum of B.S. spectrometer was set at 593 nm and then at 511 nm and TL was recorded successively. The glow curves so obtained are shown in Fig. 5.5 for $E_3$ and $E_9$ samples. These glow curves resemble closely those recorded by taking total light sum from the same sample as is clear on comparison of Fig. 6.5 with Fig. 6.2 (D and H).

(c) Kinetics of luminescence and activation energies — In the present study an attempt has been made to find the order of kinetics on the basis of geometrical shape factor of glow curves and method due to Muntoni et al. 32

The geometrical shape factor $Mg' = \frac{5}{W}$ calculated for different samples shows that its value varies from 0.47 to 0.57.

Method proposed by Muntoni et al. 32 was also followed for determining the order of kinetics. According to this method a plot of $\log \frac{I(T)}{[S(T)]^\alpha}$ versus $1/T$ results in a straight line for a specific value of $\alpha$ which represents the order of kinetics, while for other values, it is concave or convex. $S(T)$ is the integrated area of the curve from $T$ to $T_f$. $T_f$ being the temperature corresponding to the end of the glow peak. Fig. 6.6 shows the plot of $\log \frac{I(T)}{[S(T)]^\alpha}$ versus $1/T$ for few samples corresponding to first glow peak. This plot is linear for $E_4$ and $E_{10}$ phosphors corresponding to $\alpha = 1.5$ and 1.6 respectively. The value of $\alpha$ was found to lie between 1.5 and 2.0 for all phosphors in the present
Figure 6.5 - Glow Curves of $E_5$ & $E_9$ Phosphors at (a) 593 nm, (b) 611 nm Emission Wavelength under X-ray Excitation.
FIG: 6.6[A]- CURVES TO ASCERTAIN ORDER OF KINETICS OF ZnO : MgO (6:4) : Eu PHOSPHOR
FIG. 6.6 (B) - CURVES TO ASCERTAIN ORDER OF KINETICS OF MgO:Eu PHOSPHOR.
study. Such non-integer values were also obtained by the number of workers. 32, 52

In the present study activation energies were calculated by Randall and Wilkins, Gross wiener, Halperin and Briner and R. Chen's methods. Activation energies for some samples were also calculated by the method due to Muntuni et al. (based on the slope of linear plot corresponding to a particular value of $\alpha$) and listed in Table 5.3. It is observed that values obtained by this method are nearer to those calculated by assuming II order or general order kinetics.

In order to calculate the activation energies by these methods, it is necessary that all glow peaks be isolated. This isolation is done by the method of thermal cleaning as described earlier in Section 5.6.

In order to calculate activation energies corresponding to II glow peak, the total half width ($\%$) was calculated from equations (5.34) and (5.35) and then $\mu_{g'}$ was found assuming the possibility of both orders of kinetics. The value of activation energy was calculated using different formulae, assuming individually I and II order kinetics.

The values of activation energies calculated are listed in Tables 6.1 to 5.3.

All these results have been discussed in the concluding Chapter.
Table 6.1 (A)

Trapping parameters of first TL glow peak of E - Series

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>$T_m$ (°K)</th>
<th>$\alpha' = \frac{\delta}{W}$</th>
<th>Activation energies assuming I order kinetics</th>
<th>Activation energies assuming R. Chen's general order kinetics</th>
<th>Activation energies assuming II order kinetics</th>
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<tr>
<td></td>
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<td>Randall &amp; Wilkins S = 10$^9$</td>
<td>Grosswiener formula corrected by R. Chen (6.39)</td>
<td>Halperin &amp; Briner formula corrected by R. Chen (6.48)</td>
<td></td>
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<tr>
<td>E$_2$</td>
<td>356</td>
<td>0.48</td>
<td>0.64</td>
<td>0.57</td>
<td>0.63</td>
</tr>
<tr>
<td>E$_3$</td>
<td>356</td>
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<td>0.64</td>
<td>0.57</td>
<td>0.65</td>
</tr>
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<td>E$_4$</td>
<td>355</td>
<td>0.52</td>
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<td>0.51</td>
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</tr>
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<td>E$_5$</td>
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<td>E$_6$</td>
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<td>0.53</td>
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<td>Sample No.</td>
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<td>$\mu^* = \frac{S}{W}$</td>
<td>Activation energies assuming 1st order kinetics</td>
<td>Activation energies assuming R. Chen's general order kinetics</td>
<td>Activation energies assuming 2nd order kinetics</td>
</tr>
<tr>
<td>------------</td>
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<td>-----------------------------------------------</td>
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<td>Randall &amp; Wilkins</td>
<td>Grosswiener formula corrected by R. Chen (6.39)</td>
<td>Halperin &amp; Briner formula corrected by R. Chen (6.48)</td>
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<td>$X_0$</td>
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<td>$X_3$</td>
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<td>$X_4$</td>
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</tr>
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<td>0.64</td>
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<td>0.64</td>
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Table 6.2 (A)

Trapping parameters of second glow of E Series

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<th>Sample No.</th>
<th>Tm (°K)</th>
<th>$\mu g$</th>
<th>$\Delta$</th>
<th>Activation energy by Randall and Wilkins formula (6.13)</th>
<th>Activation energies assuming 2nd order kinetics</th>
<th>Activation energies from R. Chen's general order kinetics</th>
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<td>Grosswiener and Braner formula corrected by R. Chen (6.40)</td>
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<td>0.75</td>
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E_C (6.56)  E_0 (6.57)  E_W (6.58)
### Table 6.2 (B)

Trapping parameters of second glow peak of X-Series and es<sub>x</sub> - Series

<table>
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<tr>
<th>Sample No:</th>
<th>T&lt;sub&gt;q&lt;/sub&gt; (°K)</th>
<th>μ&lt;sub&gt;n&lt;/sub&gt; = ½ \frac{\delta}{W} (W calculated assuming II order kinetics)</th>
<th>Activation energy by Randall and Wilkins formula (S = 10^9)</th>
<th>Activation energies assuming II order kinetics</th>
<th>Activation energies from R. Chen's general order kinetics</th>
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<tr>
<td></td>
<td></td>
<td></td>
<td>(E_0)</td>
<td>(E_0)</td>
<td>(E_\infty)</td>
</tr>
<tr>
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<td>405</td>
<td>0.52</td>
<td>0.72</td>
<td>1.02</td>
<td>1.03</td>
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<tr>
<td>(x_1)</td>
<td>405</td>
<td>0.51</td>
<td>0.72</td>
<td>1.07</td>
<td>1.09</td>
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<tr>
<td>(x_2)</td>
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<td>0.52</td>
<td>0.73</td>
<td>0.83</td>
<td>0.82</td>
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<td>0.52</td>
<td>0.72</td>
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<td>0.73</td>
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<tr>
<td>(es_4)</td>
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<td>0.74</td>
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<tr>
<td>(es_5)</td>
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<td>0.52</td>
<td>0.74</td>
<td>0.79</td>
<td>0.78</td>
</tr>
<tr>
<td>Sample No.</td>
<td>$T_m$ (°K)</td>
<td>$N_{e}^N = \frac{S}{W}$</td>
<td>Activation energies assuming I order kinetics</td>
<td>Activation energies assuming R. Chen's general order kinetics</td>
<td>Activation energies assuming II order kinetics</td>
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<td>E₂</td>
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<td>E₄</td>
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