CHAPTER IV

THERMOLUMINESCENCE
4.1 INTRODUCTION:

Decay studies are usually performed at constant temperature and all the traps are not emptied even at the end of measurements. Hence, decay studies alone cannot provide complete information about the nature and distribution of trapping states and about the specific mechanism involved in the process of luminescence. However, one can have all this information if one supplements the decay studies by other such as thermoluminescence, photoconductivity, infra-red stimulation etc.

When a luminescent material, which has been previously excited at low temperature, is heated after removal of excitation, emission of light results; the phenomenon being known as "thermoluminescence". It is essentially the same process as phosphorescence, thermal energy is responsible for the liberation of trapped electrons or holes in both the cases. The only difference is that phosphorescence occurs at a certain fixed temperature while in thermoluminescence, the temperature changes.

The basic understanding of the thermoluminescence (TL) mechanism involves the identification of the trapping centres and recombination centres for the observed light emission.
Usually, in the thermoluminescence process, the phosphor is excited at a fixed low temperature to fill all the empty traps and then it is allowed to decay for a while so that the shallower traps will be emptied and only the deeper traps remain filled. Then the phosphor is heated at a constant rate in the dark. The filled traps due to excitation process will be emptied releasing the trapped electrons. The plot of luminescence intensity versus temperature is known as a glow curve. Hence thermoluminescence is an efficient technique to reveal information about the deeper traps and provides a better understanding about the exact nature of the trapping states\(^{(1-3)}\).

4.2 THEORIES OF TL:

The first method for calculating activation energy from TL curves was given by Urbach\(^{(4)}\), who found empirically that a reasonable estimate for the trap energy \(E\) (in eV) is given by,

\[
E = \frac{T_m}{500}
\]

where \(T_m\) is the temperature of the glow curve maximum in °K. The first theoretical treatment for a well isolated TL peak was given by Randall and Wilkins\(^{(5)}\), who assumed no retrapping and a TL intensity proportional to the rate of change of the concentration of trapped electrons i.e. monomolecular kinetics.
The relation is

\[
I = \frac{dn}{dt} = -cns \exp(-E/kT)
\]

or

\[
\frac{dn}{n} = -cs \exp(-E/kT) \, dt \quad \text{(4.1)}
\]

where \(I\) is the TL intensity, \(s\) is a constant (having the dimension of sec\(^{-1}\)) called the "escape-frequency factor" or sometimes just the "pre-exponential factor", \(n\) is the concentration of trapped electrons per c.c., \(T\) is the absolute temperature, \(k\) is the Boltzmann's constant and \(c\) is a proportionality factor which can be set equal to unity without any loss in generality. The solution of the differential equation (4.1) is

\[
n = n_o \exp \left[ -\left(\frac{S}{\beta}\right) \int_{T_0}^{T} \exp(-E/kT) \, dT \right] \quad \text{(4.2)}
\]

where \(n_o\) is the initial concentration and \(\text{deg/sec.}\) is the uniform heating rate. This gives (assuming \(c = 1\)), for TL intensity,

\[
I = n_o S \exp(-E/kT) \exp \left[ -\left(\frac{S}{\beta}\right) \int_{T_0}^{T} \exp(-E/kT) \, dT \right] \quad \text{(4.3)}
\]

(If one has some estimate for the value of \(S\), this should serve as a transcendental equation to be solved numerically to give the complete glow curve.)
By differentiating and equating to zero, one finds the condition for the maximum:

\[ \frac{\beta E}{k T_m^2} = S \exp \left( - \frac{E}{k T_m} \right) \quad \text{---- (4.4)} \]

or \( E = k T_m \left[ \log \left( 1 + f(s, \beta) \right) \right] \log s \)

where \( f(s, \beta) = \log \left( \frac{k T_m^2 / \beta E}{\log s} \right) \)

\( f(s, \beta) \) is a correction factor of the order of 0.1. Neglecting \( f(s, \beta) \) the equation (4.4) reduces to

\[ E = k T_m \log s \]

Another approximation, more suitable for some of the glow peaks, was given by Garlic and Gibson \(^6\), and is represented by the following equation,

\[ I = - \frac{dn}{dt} = S' n^2 \exp \left( - \frac{E}{k T} \right) \quad \text{---- (4.5)} \]

where \( S' \) is a constant with dimensions of \( \text{cm}^3 \text{ sec}^{-1} \). This case is usually referred to as "second order kinetics" whereas the previous corresponds to "first order kinetics". According to Garlic and Gibson, the second order approximation applies when retrapping and recombination probabilities are equal.
The solution of (4.5) is

\[ I = n_o^2 S' \exp(-E/kT) \left[ 1 + \left( n_o S'/\beta \right) \int_{T_0}^{T} \exp(-E/kT) \, dT \right]^{-2} \]

\[ (4.6) \]

The term in brackets in (4.6), as well as the right hand exponential term in (4.3), varies only slightly at temperature low in comparison to \( T_m \). Therefore, in this region, \( I \) is proportional to \( \exp(-E/kT) \). This provides a simple means for calculating the activation energy from the slope derived from a plot of \( \log(I) \) versus \( 1/T \) in the initial rise region (6,7). The initial rise method is expected to be valid for intermediate order kinetics as well\(^{(8)}\). However, some theoretical\(^{(9,10)}\), as well as experimental\(^{(11)}\) reasons limit its use.

A number of methods for calculating activation energies are based on measurement of \( T_m \), the temperature at the maximum and \( T_1 \) and \( T_2 \), the first and second-half intensity temperatures. The formulae for finding the energies by these methods usually contain one of the following factors: (a) \( \Gamma = T_m - T_1 \), 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, or (c) \( W = T_2 - T_1 \), the total half-width. By assuming that the area of the half peak toward the fall off is equal to the area of a triangle having the same height and
half-width, Lushchik\textsuperscript{(12)} showed that the activation energy can be given by

\[ E = k \frac{T_m^2}{\delta} \quad \text{---- (4.7)} \]

Once \( E \) is calculated by any method, insertion into equation (4.4) gives the value of the pre-exponential factor, as \( E \)

\[ s = \left( \frac{\beta}{\delta} \right) \exp \left( \frac{T_m}{\delta} \right) \quad \text{---- (4.8)} \]

This gives \( s \) directly. For second order kinetics, Lushchik found by the same assumption

\[ E = 2 k \frac{T_m^2}{\delta} \quad \text{---- (4.9)} \]

Halperin and Briner\textsuperscript{(8)} found two general equations for evaluating the activation energy, one for carriers raised into a level within the forbidden gap,

\[ E = \left( \frac{q}{\delta} \right) k T_m^2 \quad \text{---- (4.10)} \]

and another for excitation into the band

\[ E = \left( \frac{q}{\delta} \right) k T_m^2 \left( 1 - \Delta \right) \quad \text{---- (4.11)} \]

where \( \Delta = 2 k \frac{T_m^2}{E} \), is a correction factor, usually of the order of magnitude of 0.1. The value of \( q \) depends on the order of the process and can be found accurately only for strict first- or second-order kinetics\textsuperscript{(13)}. 
Halperin and Braner (loc.cit.) have also shown that a method based on the value of $T$ is expected to be more accurate in many cases.

Another method using the value of $T$ was given by Grosswiener (14) who found

$$E = 1.51 \frac{k}{T_m} \frac{T_1}{T}$$ \hspace{1cm} (4.12)

which he claims to be accurate to better than 5%.

Dussel and Bube (15) showed that Grosswiener's method for $E$ is out by about 7% and gave some other similar formulae for $E$. Keating (16), following other investigators (17,18), introduced the possibility of temperature dependent frequency factor $S = S^n T^a$ where $-2 \leq a \leq 2$. For all values of $a$, Keating gave the following formulae for first order peaks.

$$k \frac{T_m}{E} = (1.2 - 0.54) \frac{W}{T_m} + 0.0055 - \left[ \frac{1}{2} (\gamma - 0.75) \right]^2$$ \hspace{1cm} (4.13)

from which $E$ can be calculated. Here $\gamma = S/T$. 

Chen (19) used a combination of theoretical and empirical-computational analysis to give corrected formulae for some of the previous methods. Apart from this, he also suggested a new method of calculating $E$, based on the measurement of
total half-width \( W \).

Activation energies corresponding to each glow peak can be found by applying Chen's formulae for the general order kinetics\(^{(20)}\), (as these require no a-priori assumption as to the order of kinetics):

\[
E \frac{T}{\text{T}_{\text{m}}} = \left[ 1.51 + 3.0 \left( \frac{h}{T} - 0.42 \right) \right] \frac{kT_{\text{m}}^2}{\gamma} - 1.58 + 4.2 \left( \frac{h}{T} - 0.42 \right) \times 2kT_{\text{m}} \quad (4.14)
\]

\[
E_s = \left[ 0.976 + 7.3 \left( \frac{h}{T} - 0.42 \right) \right] \frac{kT_{\text{m}}^2}{\gamma} \quad (4.15)
\]

\[
E_w = \left[ 2.52 + 10.2 \left( \frac{h}{T} - 0.42 \right) \right] \frac{kT_{\text{m}}^2}{W} - 2kT_{\text{m}}^2 \quad (4.16)
\]

where \( \frac{h}{T} \) is the geometrical or shape factor, \( \frac{h}{T} = \frac{S}{W} \).

The pre-exponential factor corresponding to each glow peak can be obtained using Chen's formulae\(^{(19)}\):

\[
S = \left( -\frac{2.67}{W} \right) \frac{B}{10^{T_{\text{m}}/W}} \quad \text{for first order kinetics,}
\]

\[
S' \nu_0 = \frac{B \left( E/kT_{\text{m}} \right)^2 \exp \left( E/kT_{\text{m}} \right)}{T_{\text{m}} \left( E/kT_{\text{m}} + 2 \right)} \quad \text{for second order kinetics,}
\]

\[
(4.17)
\]

\[
(4.18)
\]
where $S$ and $S' n_0$ are supposed to be independent of temperature and $\beta$ is the linear heating rate. The method can also be extended to the cases where the pre-exponential factor is temperature dependent.

4.3 EXPERIMENTAL METHOD:

The experimental techniques for glow curve measurements are essentially the same as those used for phosphorescence decay with an additional provision for heating the phosphor at an uniform rate and appropriate arrangements for thermal insulation. Rate of heating, however, appears to be an important parameter. Slow rate of heating increases the resolution of glow curves\(^{(21,22)}\), whereas the higher rates ensure a sharp maxima in the glow curve which reduces the uncertainty in its position\(^{(5,6)}\). In any case, extremely low values of heating rates should be avoided as then there exists a possibility of thermal leakage which may invalidate the condition of 'frozen in luminescence'. Experimental arrangements used by some of the workers are described below.

Randall and Wilkins\(^{(5)}\) spread a thin layer of powdered phosphor on the surface of a small copper box smeared slightly with glycerol. An electric heating coil was arranged inside it and a copper-constant thermocouple was soldered to its surface. Liquid air could be poured into a funnel attached to
the box for obtaining low temperature. The method, though convenient, had the disadvantage that the rate of warming varied considerably with temperature. In the alternative arrangement, the whole box was immersed in a beaker full of liquid air, which appeared to be more satisfactory. The apparatus was further modified and as a result warming rates up to $5^\circ K/sec.$ could easily be obtained$^{(23)}$. The glow intensity was measured with a photomultiplier and a galvanometer.

Bonfiglioli$^{(24)}$ studied the glow of $F$ centres in alkali halides with the following arrangement. The oven constituted a large plate of copper covered with a layer of evaporated platinium to avoid oxidation. The sample was kept inside a small well in the centre along the axis of the plate. Temperature was recorded by a pt/pt-Rh thermocouple located at a definite position under the specimen, while the glow intensity was detected with RCA Ip 21 or Lp 28 photomultiplier and a photographic paper fixed on to a rotating drum.

Halperin et al.$^{(25)}$ mounted an alkali halide crystal in a vacuum crystal. This could be heated up from the liquid air temperature to about $600^\circ K$ with the help of a heating element. The light emitted by the crystal reached the detector (RCA Lp 28 photomultiplier) through a quartz window in the cryostat. The output from the amplifier$^{(26)}$ was fed to a 50 mV Brown Recorder, on which the glow curves were recorded. Temperature
was measured with a calibrated copper-constantan thermocouple with one junction fixed near the crystal and the other in an ice bath. The heating rate could be varied between 10⁰K to 20⁰K per min. and the temperature could be fixed with an accuracy of about 0.2 degree.

4.4 PRESENT METHOD:

The apparatus used in the present investigation is shown in Fig. 4.1. It has been designed in these laboratories and consists of a box made of copper sheet. The box is divided into two chambers. The lower chamber has a long cylindrical cavity of copper. In this cavity the phosphor is kept in a metallic phosphor holder A which just fits in the cavity. The cavity is surrounded by copper tubing E F through which water can be passed for cooling. A heater coil is wound round the cavity, the two ends of which are brought out of the chamber to the terminals Q and R. Two openings G and H serve as inlet and outlet for compressed air.

The upper part of the chamber has a slide door I and the cavity in the lower chamber opens in this chamber at the base. In the upper part a slide assembly J is fixed at the top. This consists of a metallic cylinder K of the same diameter as the cavity in the lower chamber and it is fixed against an opening in the plate J. The top lid of the upper
FIGURE 4.1

Thermoluminescence Apparatus.

1. A - Perlite Sheet Box
2. B - Photo Tube
3. C - Cable to Control Panel
4. D - Threaded Metallic Tube
5. E - Slide Assembly
6. F - Metallic Cylinder
7. G - Slide Door
8. H - Copper Tubing
9. I & J - Heater Coil
10. K - Heater Coil Terminal
11. L - Metallic Cup
12. M - Opening for Compressed Air
13. N - Base Plate
14. O - Ammeter
15. P - Stabilized A.C.
chamber has an opening to which a threaded metallic tube L is fixed. To this tube L, photomultiplier 1p 21 is screwed. By sliding the plate J, the photomultiplier can be exposed to the phosphor sample or shielded.

The glow intensity was measured with the help of a galvanometer as in the case of phosphorescence decay studies discussed in the preceding chapter. The corresponding temperature was obtained from a calibration curve.

For calibration of heater the phosphor holder A was filled with mercury and one junction of a copper-constantan thermocouple was immersed in it while the other junction was kept in cold water. The current which was to be used in the final studies was pressed through the coil. The galvanometer deflection as a function of temperature was plotted. Another curve was plotted between the galvanometer deflection and the time of heating. With the help of these two graphs, a third graph between temperature and time was plotted which was used as a calibration graph. This calibration curve for the warming rate of 1.0°K/sec. is shown in figure 4.2.

4.5 GLOW CURVES:

The phosphor was filled up to a fixed marked in the phosphor holder A and it was excited for five minutes with an U.V. lamp in a similar way as in the decay studies. The
CURRENT = 2.8 AMP

HEATING RATE \( \beta = 100 \text{ °K/SEC} \)
phosphor holder was then gently placed in the cavity of the apparatus. The plate J was slid inside so that the cylinder K just comes in the line with the phosphor sample, and the photomultiplier. The excited phosphor was allowed to decay till the intensity reduced to very low value. The heater current was switched on. The galvanometer deflection was noted as a function of time and with the help of the calibration graph the glow curves were plotted with a heating rate of $1.0^\circ$K/sec.

4.6 RESULTS:

The glow curves are shown in figure 4.3. The studies were carried out from $300^\circ$K to about $400^\circ$K.

The glow curves obtained in the present investigations show only one peak in all the phosphor samples. There is an appreciable and regular variation of peak temperature with the variation of relative quantities of CaS and SrS. The peak temperature gradually decreases with increasing ratio of SrS to CaS. The peak temperature for CaS is $395^\circ$K and for SrS, it is $345^\circ$K.

The relative intensity of the peak is maximum for CaS, it is a minimum for SrS. The relative intensity gradually decreases in accordance with the increasing ratio of SrS to CaS.
The activation energies ($E_T$, $E_o$, and $E_w$) were calculated using Chen's formulae 4.14, 4.15, 4.16. These are being given in Table 4.1. The values of the shape factor also are given in the same table in column 2. According to Chen, a value of $f_3 \approx 0.42$ suggests first order kinetics and $f_3 \approx 0.52$ suggests second order kinetics. The factor 's' is also evaluated for each sample and are shown in Table 4.1 in column 4. It is found that 's' in general decreases as the concentration of SrS increases. The value of trap depth is also calculated using Randall and Wilkins formula $E = kT_m \log s$. These are shown in Table 4.2. Table 4.3 gives the mean values of $E$ as obtained from Chen's formulae, the values of $E$ obtained from Randall and Wilkins formula and that from the first exponential obtained from 'peeling off' procedure of decay curves.
Table 4.1
Trap depth calculated by using Chen's formulae

\[ s = 10^9/\text{sec}. \]

Heating Rate = 1.0^\circ\text{K/sec.}

(Current flown through the heater of the apparatus = 2.8 Amps.)

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Shape-factor (µg)</th>
<th>Peak Temp. (^\circ\text{K})</th>
<th>'s' (\times 10^9)</th>
<th>Trap Depth (eV)</th>
<th>(E_w)</th>
<th>(E_t)</th>
<th>(E_b)</th>
<th>Average</th>
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Table 4.2

Trap depth calculated by using Randall & Wilkins' formula

\[ s = 10^9 \text{/sec.} \]

Heating Rate \( = 1.0^\circ \text{K/sec.} \)

(Current flow through the heater of the apparatus \( = 2.8 \text{ Amps.} \))

<table>
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<tr>
<th>Sample No.</th>
<th>Peak Temperature</th>
<th>Trap Depth (eV)</th>
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<td>0.52</td>
</tr>
<tr>
<td>11</td>
<td>345</td>
<td>0.50</td>
</tr>
<tr>
<td>Sample No.</td>
<td>Peak Temp. (°K)</td>
<td>Average Trap Depth by Chen’s formulae (eV)</td>
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<td>-----------</td>
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<td>----------------------------------------</td>
</tr>
<tr>
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REFERENCES


