CHAPTER - IV

THERMOLUMINESCENCE

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4.1 INTRODUCTION

Thermoluminescence (TL) has been extensively used as a technique for elucidating qualitatively the nature of electron traps and the trapping process involved in phosphors. The luminescence process in which the stored energy in the suitably excited phosphor is realesed in the form of luminescent emission, after supply of thermal energy is known as thermoluminescence. The intensity of the luminescent emission is to be measured as a function of temperature. A glow curve is plotted between intensity against temp. The glow curves is used for the estimation of activation energy (E) and escape frequency factor (S). As both E and S depend sensitively upon the trapping centres, glow curve can give valuable information about the role of various impurities present in the sample.

The object of present investigation is to analyse the observed glow curves for samples containing varying concentration, of Mn , Bi and Dy , Tb as to get the following information of the prepared phosphors.

i) The effect of activators on general features of glow curves and on trap distribution.

ii) The distribution of trapping levels.

iii) The values of escape frequency

iv) The size of traps

v) The type of kinetics involved in TL process

vi) The dose dependdnce of TL glow peak.

4.2 THEORY OF GLOW CURVES

4.2.1 TL-glow curve parameters :

The simplest and commonly used technique for studying the TL glow curves is ~~the~~ one suggested by Urbach (12) and Randall and Wilkins(31);

For the calculation of TL intensity, it is presumed that the trapped electrons have maxwellian distribution of thermal energies and that probability 'p' for the thermal release of trapped electron form the trapper unit time is given by -

$$P = S\ e^{-(E/KT)} \qquad .. \qquad (4.1)$$

So that, TL intensity is given by

$$It \propto n_t . p \qquad .. \qquad (4.2)$$

where T = absolute temp.

K = Boltzmann's constant

E = trap depth or activation energy

S = constant having the dimensions of frequency.

nt = number of filled traps at time 't'

't' and 'T' are related to heating rate β by

$$\beta = \frac{dT}{dt} \qquad .. \qquad (4.3)$$

In the simplest case, the factor 's' is connected with the capture cross section S_T of trap given by

$$S = Vc\ Nc\ S_T \qquad .. \qquad (4.4)$$

where Vc = thermal velocity of electron in conduction band

Nc = density of available trap levels.

In a physical sense, however, one can regard the trap as a potential well, in which case 's' can be expressed in terms of product of number of times an electron hits the wall and the wall reflection coefficient. It then follows that values of should be of the order of or less than the vibrational frequency of the crystal (27). However, in practice, one dose come across situation does where 's' takes values differing from lattice phonon frequencies by many order of magnitude. This is attributed to fluctuation in local environment of the trap such as produced by a nearby impurity, causing changes in the frequency of localised phonons.

4.2.2 Randall and Wilkins Theory : (First order Kinetics).

Randall and Wilkins (31) have given a simplest mathematical representation for the luminescence glow peaks without any overlaping, The basic assumptions made are -

i) an injection of electron is the only rate determining process.

ii) radiation-less transition and probability of retrapping is negligible.

iii) The life time τ for recombination is so small that $\frac{dn}{dt} << n/\tau$ with 'n' as concentration of electrons in conduction band.

iv) Glow peaks arising from traps of different depths do not overlap

With these assumptions they obtained an expression for variation of TL intensity with temperature.

The luminescence intensity at any time is directly proportional to the rate at which detrapping occurs. During the heating, if n is the concentration of filled traps at any time 't' (temp. T) then intensity of TL is given by,

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

or

$$I = - c \frac{dn}{dt}$$

$$= - C P n$$

$$= - Cn S e^{- E/KT} \qquad .. \quad (4.5)$$

where n is number of trapped charge carriers (electrons & holes) and c is constant.

$$\therefore \frac{dn}{n} = - C . s . e^{-E/KT} . \frac{dt}{dT} dT$$

$$= - C \frac{S}{\beta} e^{-E/KT} . dT$$

where $\beta = \frac{dT}{dt}$ .. (4.6)

by integrating and substituting in equation (4.5) the TL intensity turns out to be

$$I = n_o C_{se}^{-E/KT} \exp. \left[- \int_o^T \frac{S}{B} e^{-E/KT'} dt \right] \quad .. \ (4.7)$$

where n_o is the initial number of trapped carriers. It is easily seen that the intensity builds up as T increases, reaches maximum for particular value of T = Tm and then falls off for further increase in temp.

By setting dI/dT = 0 at T = Tm one obtain the important relationship

$$\frac{BE}{K\ Tm^2} = S \cdot e^{-E/KTm} \quad .. \quad (4.8)$$

At a fixed temperature T, Csexp (-E/KT) is a constant, say A. Equation (4.5) can thus be written as $\frac{dn}{n} = -A\, dt$ which on integration gives

$$n = n_o\, e^{-At} \quad .. \quad (4.9)$$

from equation (4.5) and (4.8)

$$I = I_o\, e^{-At} \text{ where } Io = Ano \quad .. \quad (4.10)$$

Thus when at a fixed temperature T the TL intensity decays exponentially, the TL process is said to be followed the First Order Kinetics.

4.2.3 Garlick and Gibson theory : (Second order Kinetics)

Garlick and Gibson (13) exten-ded the Randall and Wilkins theory by considering the equal probabilities for the retrapping and recombination of released electrons.

If N is the total number of traps per cm^3 of which n are filled at a time t, the probability that a carrier will go to the recombination centre is _

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

Therefore, $I = C\,\frac{dn}{dt} \cdot \frac{n}{N}$

$$= - C\,\frac{n^2}{N}\,s\,e^{-E/KT} \qquad .. \quad (4.11)$$

By integrating equation (4.11) and rearranging, TL intensity is obtained as-

$$I = \frac{n_o^2\;C\,S'\,e^{-E/KT}}{\left[1 + S'\,\frac{n_o}{\beta}\int_o^T \exp.(-E/KT')\,dT'\right]} \qquad .. \quad (4.12)$$

where $S' = \frac{S}{N}$ is called the pre-exponential constant and has the unit ($cm^3 \cdot sec^{-1}$).

At a fixed temperature T, equation for TL intensity can be derived as

$$I = \frac{I_o}{(1 + A'n_o t)^2} \qquad .. \quad (4.13)$$

A straight line graph obtained by plotting $I^{-\frac{1}{2}}$ against time provides a test for applicability of second order kinetics in TL-process.

4.2.4 General Order Kinetics

A fundamental approach to this was developed by Braunlich and co-workers (2, 19)

Fig. 4.13 depicts a simple band picture of a phosphor containing localised energy levels in the forbidden gap. For simplicity only two kinds of electron traps are assumed to be present corresponding to the energy level E_1 and E_2 and one recombination level E_3. Excitation of phosphors populates levels E_1 & E_2 with electron while E_3 traps holes from the valence band. The thermal depopulation of shallow trap at E_1 with deeper trap of E_2 lying dormant leads to the active regime of an isolated TL peak.

If the electrons are released into the conduction band we have model I. If they are raised to an excited state E, We have model II. Let us define the following symbols for various parameters of this model.

N_1 = Concentration of traps at energy level E_1
N_2 = Concentration of traps at energy level E_2
N_3 = Concentration of traps at energy level E_3
n_1 = Concentration of electrons in trap at E_1
n_2 = Concentration of electrons in traps at E_2
N_c = Concentration of electron in the conduction band.
N_v = Concentration of holes in the valance band
(assumed to be zero)
P = probability per second of the electron release from traps E_1 given by
$P = S \exp. (- E/KT)$ where E is trap depth of level E
$E = E_9 - E_1$ for model I
$E = E' - E_1$ for model II
q is retrapping coefficient, R = recombination coefficient as introduced in following rate equation
Model I : see fig. 4.13.

The rate at which the concentration of trapped electrons and conduction electron vary are given by

$$\dot{n}_1 = -P_{n1} + q \; n_c \; (N - n_1) \quad \text{----(4.14)}$$

$$\dot{n}_c = \dot{n}_1 R \, n_c \, N_3 \quad \text{---- (4.15)}$$

The charge balance gives

$$N_3 = n_1 + n_2 + n_c \quad \text{-------(4.16)}$$

The differential equations are analytically untraceable without the following simplifying assumptions.

$$\dot{n}_c << \dot{n}_1 \quad \text{and} \quad n_c << n_1 \quad .. \quad (4.17)$$

Justification of these assumptions is to be found in the work of Kelly et al (19) and Shenkar and Chen (33) who obtained numerical solutions of the equation to check the assumptions. With these assumptions, the rate equation are readily integrated to yield the density of trapped electron as a function of temperature when linear heating program $\beta = t$ is used.

$$\left(1 - \frac{FN_1}{N_2}\right) \ln x - F\left(1 + \frac{N_1}{N_2}\right) \ln \frac{n_1 + N_2}{n_o + N_2} + \int_{T_o}^{T} \frac{s}{\beta} \, e^{-E/kT'} \, dT' = 0 \quad .. \quad (4.18)$$

which reduces when N_2 is negligible to

$$(1-F) \ln x + \frac{F}{y}\left(1 - \frac{1}{x}\right) + \frac{s}{\beta} \int_{T_o}^{T} e^{-E/KT'} \, dT' = 0 \quad .. \quad (4.19)$$

when $x = \frac{n_1}{n_o}$, $y = \frac{n_o}{N_1}$, $F = \frac{q}{R}$

n_o being the density of electrons on traps E_1 at the initial temp. T the thermoluminescence intensity. I, for model - I given by

$$I_1 = \frac{P(n_1^2 - n_1 n_2)}{N_2 + FN_1 + (1-F)\, n} \quad .. \quad (4.20)$$

With n_1 given by the solution (4.18) or (4.19). The theoretical glow curve can be constructed by (4.20) For any set of model parameter E, S, F, n_o, N_1 and N_2.

The above generalised Kinetics equations reduce to first order and second order cases when F = 0 and F = 1 respt.

Model II : The trapped electrons are taken to the excited state E' from which they tunnel to recombination centres. The rate equation given by Mukti (25). The theoretical glow curves for this model can be obtained from the following two equations ;

$$\left(1 + \frac{S}{FN_2}\right)\ln x - \frac{S}{FN_2} \ln \frac{n_1 + N_2}{n_o + N_2} + \int_{T_o}^{T} \frac{P}{\beta}\, dT' = 0 \quad \text{---} \quad (4.21)$$

$$\text{and } I_2 = \frac{Pn_1^2}{n_1} = \frac{S}{\beta F} \quad .. \quad (4.22)$$

while applying model I of the above approach to determine the TL parameters, Braunlich (3) and Shenkar and Chen (33) showed the dependance of the obtained values on thetrap occupancy. Shenkar and Chen in particularly demonstrated by computation that the term 'Kinetics Order' may become mean-ing-less if the inequality,

$$RN_3 > q\,(N_1 - n_1) \quad \text{or} \quad RN_3 < q\,(N_1 - n_1)$$

changes direction during the TL glow peak emission.

4.3 METHODS FOR DETERMINING TRAP DEPTH:

There exist several methods for determination of trap depth from glow curves. In this section method are divided into three groups (i) Method making use of shape of glow curve (ii) Method making use of various heating rate (iii) Other Methods.

4.3.1 Methods making use of shape of glow curve

Fig. 4.1 representsa general shape of glow curve defining some characteristic quantities such as Tm, T_2, δ , W etc. It can be approximated by a triangle. This principle has been used for the derivation of several expressionsfor the trap depth, as method using high temperature side of the glow peak :(after Luschik (20).

This is based on the shape of glow peak whose symmetry is dependent upon both the transition probabilities and on the number of traps compared to that of luminescence centres. By assuming that the area of the half peak towards the fall off is equal to the area of triangle having the same height and half width, Luschik (20) showed that the activation energy for the first order Kinetics is given by -

$$E = \frac{KTm^2}{T_2 - T_m} \quad .. \quad (4.23)$$

Under the same assumption he obtained an equation for the second order kinetics and is

$$E = \frac{2KTm^2}{T_2 - Tm} \quad .. \quad (4.24)$$

In the above equations, Tm is glow peak temperature and T2 is temp. on high temp. side of glow peak at which intensity falls off to half of its peak value.

Chen (32) has suggested empirical correction factors of 0.976 and 0.853 for First Order and Second Order Kinetics respectively. Thus we have,

$$E = 0.976 \frac{KTm^2}{T_2 - Tm} \quad .. \quad (4.25)$$

For first order Kinetics

and

$$E = 1.706 \frac{KTm^2}{T_2 - Tm} \quad .. \quad (4.26)$$

For second order Kinetics.

b) Method Using Low temperature side of the glow peak : (After Halperin and Braner)

In this method, the symmetry of glow peak about its maximum is used for calculation of activation energy. Halperin and Braner(16,17) considered the luminescence emission as mainly due to two kinds of recombination process. In one process (such as model I of Fig. 4.13), the electron raised to an excited state with the forbidden gap below the conduction band recombines with the hole by tunneling process and in other the recombination takes place via a conduction band (sub Model-II of fig. 4.13) If it is assumed that the ratio ρ, of the initial concentration of the trapped electrons to trapped holes is close to unity, then the thermal activation energy E, can be calculated using the appropriate equation of following :

Type of process	Equation	condition	
Tunneling	$\varrho = 1$		
a) Recombination dominant	$E_1 = \frac{KT_m^2}{T_2 - T_m}$	$\mu_g \simeq e^{-1}$	.. (4.27)
b) Retrapping dominant	$E_2 = \frac{2KT_m^2}{T_2 - T_m}$	$\mu_g \simeq 0.5$	.. (4.28)
Via conduction band	$\varrho = 1$		
a) First order Kinetic dominant	$E_3 = \frac{1.72\ KT_m^2}{(T_m - T_1)}(1 - \frac{5.16}{\Delta})$	$\mu_g \leqslant e^{-1}(1 + \frac{2}{\Delta})$	..(4.29)
b) Second order kinetic dominant	$E_4 = \frac{1KT_m^2}{T_m - T_1}(1 - \frac{6}{\Delta})$	$\mu_g \geqslant e^{-1}(1 + \frac{2}{\Delta})$	..(4.30)

where $\frac{1}{\Delta} = \frac{KT_m}{E} \ll 1$ is a correction Factor, and T_1 is the temperature on low temp. side of glow peak at which intensity is one half of its peak value. The Factor $\mu_g = \frac{\delta}{W} = \frac{T_2 - T_m}{T_2 - T_1}$ is called the symmetry factor, and is a characteristic of the type of Kinetics involved in the process.

$\mu_g \leqslant e^{-1}(1 + 2/\Delta)$ for First order Kinetics, and

$\mu_g > e^{-1}(1 + 2/\Delta)$ for second order kinetics,

Thus the advantage of this method lies in the fact that the first half of peak is sufficient for the evaluation of E and it also points a way of determining the Kinetics of the process involved. But many times, the presence of weak shoulders at the high temp. side of glow peak causes an apparant increase in the

μ_g values which may wrongly indicate the process to be of the second order (21). The disadvantage is that E has to be evaluated in an iterative manner. One has to estimate E first by assuming correction factor to be Zero, then calculate the correction factor $\frac{1}{\Delta} = \frac{KTm}{E}$ and then re-evaluate E.

When the ratio ρ is greater than unity the activation energy is given by

$$E = \frac{KTm^2}{T_2 - Tm} \left[1 + \frac{T_2 - T_1}{T_m - T_1} \right] \quad .. \quad (4.31)$$

with condition $\mu_g = 0.5$

Chen (32) has modified these formulae to avoid the interation and gave following equations for First Order Kinetics,

$$E = \frac{1.52\ KTm^2}{Tm - T_1} - 3.16KTm \quad .. \quad (4.32)$$

and for Second order Kinetics,

$$E = \frac{1.813\ K\ Tm^2}{Tm - T_1} - 4\ K\ Tm \quad .. \quad (4.33)$$

c) <u>Method using Full half width of the glow peak</u> (After Chen) :

Chen (32) has developed Mathematical equation for E which makes use of the full half width of a glow peak which can be measued with better experimental accuracy and gave following relations :

For First Order Kinetics,

$$E = 2\ K\ Tm\ \left(\frac{1.25\ Tm}{T_2 - T_1} - 1 \right) \quad .. \quad (4.34)$$

and for second order Kinetics,

$$E = 2\ K\ Tm\ \left(\frac{1.756\ Tm}{T_2 - T_1} \right) - 1 \quad .. \quad (4.35)$$

Here numerical constants are chosen emperically to have a better estimation of E and $\frac{E}{K\ Tm} \gg 1$, Moreover, Chen (6) showed that the symmetry Factor $\mu g = 0.42$ is characteristic. On correlating the symmetry Factor μg and Order of Kinetics α, he gave the following equations to evaluate E for general order Kinetics,

$$E = \left[(1.51 + 3.0\ (\mu g - 0.42)\right] \frac{KTm^2}{Tm - T_1} - \left[1.5 + 4.2(\mu g - 0.42)\right] . 2KTm \quad .. (4.36)$$

$$E = \left[0.976 + 7.3(\mu g - 0.42)\right] \frac{KTm^2}{T_2 - Tm} \quad .. (4.37)$$

$$E = \left[2.52 + 10.2\ (\mu g - 0.42)\right] \frac{KTm^2}{T_2 - Tm} - 2\ KTm \quad .. (4.38)$$

4.3.2 Methods Making use of various Heating Rates

a) Method due to Booth, Bohum and Parfianovitch -

Booth (4) Bohum (5) and Parfianovitch (30) have shown independently that the activation energy can be determined without prior knowledge of frequency Factor S, by heating the phosphor, at two different heating rates β_1 and β_2. If $\beta_1 > \beta_2$ then $Tm_1 > Tm_2$ where Tm_1 and Tm_2 are the corresponding values of glow peak temp. at two different heating rates β_1 and β_2. Eliminating S from eqn.

$E/\ KTm^2 = (S/\beta)\ \exp.\ (-E/KTm)$ they found

$$E = \frac{KTm_1\ Tm_2}{Tm_1 - Tm_2} \quad \ln \quad \frac{\beta_1\ Tm_2^2}{\beta_2\ T^2_{m_1}} \quad .. (4.39)$$

If Tm can be measured within an accuracy of $1^{\circ}k$, the method is found to yield E within an error of 5% (22).

b) Method due to Schon :

To achieve an improved accuracy in E values Schon (34) modified the eqn. (4.39) by replacing Tm^2 by $Tm^{3.5}$ which results in

$$E = \frac{K\ Tm_1 Tm_2}{Tm_1 - Tm_2} \quad \ln \quad \frac{B_1\ Tm_2^{3.5}}{B_2\ T_{m_1}^{3.5}} \quad .. (4.40)$$

c) Method due to Chen and Winer :

Consider Im to be the glow peak intensity corresponding to TL maximum obtained with heating rate β, Chen and Winer (7) have shown a plot of ln $(I_{mi}\, T_{m_1}^4 / \beta i^2)$ versus $(1/T_{mi})$. Yields a straight line with a slope equal to E/K. knowing the slope, E can be evaluted,

d) Method due to Hoogenstraten :

Hoogenstraaten (18) has shown that the glow peak temp. Tm is related to E by the equation.

$$\ln \frac{T_{mi}^{2}}{\beta i} = \frac{E}{KT_{mi}} + \ln \frac{E}{SK} \quad .. \quad (4.41)$$

Thus the plot between Ln $(T_{mi}^2/\beta i)$ and $(1/T_{mi})$ is linear with slope equal to E/K_1 from which E can be evaluated,

4.3.3 Other Methods

a) Method due to Urbach :

Urbach (37) derived independently from equation (4.7) an expression for activation energy by taking $S=10^{0}$ sec^{-1}.

The equation is

$$E = T_m / 500 \quad .. \quad (4.42)$$

b) Method due to Randall and Wilkins

Randall and Wilkins method is based on equation (4.7) which assumes monomolecular Kinetics and no retrapping. In this method Tm corresponds to a temperature little below that at which the frequency of an electron escaping the trap is one per second. This is

$$S \exp.(-E/KT_m)\left[1+F(S,\beta)\right] = 1 \quad .. \quad (4.43)$$

The Function $F(S,\beta) << 1$ and this gives the trap depth E. The equation for E is

$$E = T_m \left[1+F(S,B)\right] \cdot \quad K \log s \quad .. \quad (4.44)$$

where $F(S,\beta)$ is another function of S and β, when β lies between 0.5 and $2.5\,^{\circ}k\ sec^{-1}$ and S equals the value $2.9 \times 10^{9}\ sec^{-1}$, the above equation reduces to

$$E = 25\ KTm \quad .. \quad (4.45)$$

c) Method due to Grosswiner :

Grosswiner (14) derived an equation for determining E_1 for First Order Kinetics as -

$$E = \frac{1.51\ KTm\ T_1}{Tm - T_1} \quad .. \quad (4.46)$$

According to him this equation gives accurate results within ± 5% provided $S/\beta > 10^{7}\ ^{\circ}k^{-1}$ and $E/KTm > 20$ Chen's modific-ation to Grosswiner :

Chen modified the Grosswiner's relation emperically giving -

$$E = \frac{C_1 K T_m\ T_1}{T_m - T_1} \quad .. \quad (4.47)$$

where $C_1 = 1.41$ for first order kinetics and $C_1 = 1.68$ for second order.

d) Method due to Dussel and Bube :

Dussel and Bube (10) have shown that Grossweiner's method yields values of which are about 7% higher for an improved accuracy they suggested emperically

$$E = C_8\ \frac{K\ Tm\ T_1}{(Tm - T_1)} \quad .. \quad (4.48)$$

According to them when $\frac{E}{KTm} = 17$, 22 or 26, C8 has values 1.402, 1.415 or 1.421 respectively.

e) Method due to Garlick and Gibson : (Initial Rise Method) :

This method is independent of order of kinetics. The method of initial rise, suggested by Garlick and Gibson (13) is based on the fact that for all types or kinetics the intensity in the initial part of the glow curve can be expressed in the form

$$I = F\,e^{(-E/KT)} \qquad .. \quad (4.49)$$

E being a function of number of completely filled traps and empty centres which takes in to account the transition probabilities involved. Assuming F to be constant in initial part of glow curve the equation (4.49) takes the form :

$$\text{Log } I = \frac{-E}{KT} + \text{constant} \qquad .. \quad (4.50)$$

Hence, the plot of LnI vs $\frac{1}{T}$ (called the Arrhenius plot). for temperature well below Tm is a straight line with slope -E/K, and hence E can be evaluated. The method provides a quick analysis of initial ascending part of the glow which yields E, without any knowledge of S and is independent on recombination mechanism.

f) Method due to Nambi, Bapat and Ganguly :

Activation energy can be determined by the empirical formula developed by Nambi et al. (28) for $CaSO_4$:Re phosphors. The relation between glow peak temperature Tm and activation energy E is given by

$$E = 3.12 \times 10^{-3}\ Tm - 0.23 \quad . \qquad .. \quad (4.51)$$

g) Numerical Kinetics Method

This method of analysis (8) involves a numerical computation, which proceeds in small arbitrary steps, During each step the concentration of trapped charge, the carrier concentration, the radiative relaxation of excited centres etc. are adjusted in accordance with the physical process involved when used to analysis the experimental data, some initial approximate values of E and S are choosen and they are suitably varied to determine the values giving the best least square, fit to the experimental data.

h) Isothermal decay method

In this method, after excitation the sample is quickly heated to specific temperature and at this temperature the luminescence decay is measured. This method has the advantage that such difficulties arising form overlapping of peaks and change in quantum efficieny or the emission spectra occuring under the non-isothermal conditions are avoided. The decay curve obtained can be analysied into sum of sharply defined linear region and it has been shown (15) that for the first oder kinetics :

$$I(T) = n_o S \text{ exp. } (-E/KT) \text{. exp. } (S.t. \text{ exp. } (\frac{-E}{KT}) \quad .. \ (4.52)$$

where t is time

Taking logarithm of equation (4.52) we have,

$$\log I(T) = - S \ t \ \text{ exp. } (- \frac{E}{KT}) - \frac{E}{KT} + \log n_o S \quad .. \ (4.53)$$

Thus slope m of log I(T) versus t curve is given by

$$m = S.\text{exp. } (-E/KT) \qquad .. \ (4.54)$$

Taking the slopes M1 and M2 at at two different temp. T1 and T2 one can write -

$$\log \frac{M1}{M2} = \frac{E}{K} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \qquad .. \ (4.55)$$

which can be used to determine the activation energy E. The escape frequency factor may be found by the substitution of equation (4.55) in equation (4.54).

4.4 METHODS FOR DETERMINATION OF FREQUENCY FACTOR

The value of escape frequency factor 'S' can be obtained from photoconductivity, phosphorescence decay, dielectric relaxation measurement and thermoluminescence measurement. There exist severl methods for determinig S from TL studies and a brief survey is given below :

4.4.1 Method due to Randall and Wilkins :

Randall and Wilkins (31) for the First Order Kinetics have given the general equation

$I = - dn/dt$ with a constant heating rate β.

$$I = Sn_o \exp.(-E/KT). \exp.\left(- \frac{S}{\beta} \int_{T}^{T_o} \exp.(- \frac{E}{KT'})dT' \right. \quad .. (4.56)$$

By equating derivatives of this equation to zero, the condition for maximum of glow one obtains,

$$\frac{E}{KTm^3} = \frac{S}{\beta} \exp.(-E/KTm) \quad .. (4.57)$$

where Tm is temperature at the maximum of glow peak knowing Tm, β, and E (determined by other method) S can be calculated.

4.4.2 Method due to Garlick and Gibson :

Following the second order kinetics, the solution of equation $I = - dn/dt$ ... given by Garlick and Gibson (15) with constant heating rate β is

$$I = S' n_o^2 \exp.(-E/KT) \left(1+\frac{S'n_o}{\beta}\right) \int_{T_o}^{T} \left[\exp.(- \frac{E}{KT'}) dT'\right]^{-2} \quad ..(4.58$$

Differentiating the equation and equation the derivative to zero, the condition for maximum of peak is ,

$$1 + \frac{S'n_o}{\beta} \int_{T_o}^{Tm} \exp.(-E/KT)\, dT. = \frac{2KTm^2}{\beta E} S'n_o \exp.(-E/KTm) \quad ..(4.59$$

Assuming Tm to be the experimental peak temperature, and with all other parameters in equation (4.59) are known one can calculate the frequency factor $S = Sn_o$ for different value of E.

4.4.3 Isothermal decay Method

The method suggested by Garlick (15) for the first order kinetics points that in an isothermal decay a plot by log I versus t may be regarded as a sum of sharply defined linear region slope m given by equation. $m = S \exp.(-E/KT)$. By knowing E, the frequency factor S can be calculated using equation,

$$S = m.\exp.\ (E/KT) \qquad .. \quad (4.60)$$

4.4.4 Method due to Aramu and Maxia

The method due to Aramu and Maxia (1) starts from Kinetic equation and allows to determine the frequency factor by the use of simplified formula,

$$S = \beta.\ \exp.\ \eta \qquad .. \quad (4.61)$$

where β is heating rate and η is intercept with vertical axis of plot of log I versus 1/T. The formula is applicable for saturated glow peak and when the concentration of holes bound to luminescence centre is equal to the trapped electron concentration.

4.4.5 Method due to Curie

As suggested by Curie (9), the glow peak temp. Tm and heating rate β are related to escape frequency factor, by the equation of the type,

$$\frac{S}{\beta} = \frac{2}{\delta}\ \exp.\ \frac{2Tm}{\delta} \qquad .. \quad (4.62)$$

where $\delta = T_2 - Tm$ is high temp. half width. Once ratio of Tm/δ is known, the escape frequency factor S can be evaluated,

4.5 DETERMINATION OF SIZE OF TRAP

The capture cross-section (σ) of each type of trapping centre can be evaluated from the knowledge of escape frequency factor.

Mott and Gurney (26) proposed the following equation on the assumption that the density of free electrons (or holes in case of hole trap) is equal to the density of empty traps.

$$\frac{1/T}{\sigma} = \frac{2\pi\, m(KT)^2 \;\; \sqrt{6\pi}}{h^3} \exp.\left(-\frac{E}{KT}\right) \quad .. \; (4.63)$$

on combining this equation with equation viz.

$$P = \frac{1}{T} = S.\exp.\left(-\frac{E}{KT}\right)$$

we have a numerical equation of type,

$$\sigma = \frac{S}{1.63 \times 10^{21}.T^2}$$

which in its simplest form be given as (32)

$$\frac{S}{\sigma} = 1.5 \times 10^{26}$$

Thus value of σ can be estimated approximately.

4.6 RESULTS AND DISCUSSION

Results obtained under uv excitation for 5 minutes can be briefly stated as follows :

a) Glow Curves

The glow curves are plotted for the undoped CaS Phosphor with Mn and rare earth (Dy) as activator (fig. 4.4). The heating rate used was 2.4 °k/sec. The measurements have been carried out in the temp. range of 300°k to 593°k. From these graphs it seems that undoped CaS exhibits very weak luminescence. This may be due to defect in the crystal structure or inherent impurities present in the starting (host) material. The luminescence gets enhanced in the presence of activators Mn, Dy and Bi and Tb. However, overall shape of glow curve remains same. Typical glow curves for different samples with different concentration of Dy with Mn and Tb with Bi are as shown in the fig. 4.5 to 4.7. As seen from the graphs a single broad peak at round 613 $^{\circ}$k for the phosphor CaS:Bi:Tb and the peak at round 633 $^{\circ}$k for CaS:Mn:Dy phosphor, from shape of glow curves it seems that the peaks are not a single but it may have more than one peak. These peaks are situated close to each other and their resultant is indicated by a composite glow curve. In the present study, however, the isolated peaks are not resolved using partial bleaching technique. Calculations of activation energies from the shape of glow curve are done assuming peak to be single.

It is observed that the variation of concentration of Dy and Tb in the presence of Mn and Bi respectively has not significantly affected the shape of the glow curve. Only the peak intensity changes with concentration. Fig. 4.8 shows variation of peak intensity with conc. of Mn and Dy and also Bi with Tb. From graph it is seen that peak intensity intially increases and then decreases with conc. of Dy with Mn and again it increases. Similar change is also observed with variation of peak with change in conc. of Tb with Bi. (Fig. 4.2, 4.3. 4.9 and 4.10) show~~s~~ variation of peak intensity with concentration of activators. The table no.4.1 - gives the peak temp. and peak intensities of the prepared samples.

As from TL out put variations it seems that Mn with 0.1% and Dy with 0.001% gives maximum TL glow peak intensity. The sample MD-33 give maximum TL out put amongst the choosen concentration. Thus optimum concentration of Mn in the host seems to be around 0.1% and for Dy it is around 0.001%

Similar, TL out put variation is observed for CaS:Bi:Tb phosphor. The phosphor MD-24 with composition CaS:Bi:Tb(Bi =0.1% and Tb = 0.005%) gives maximum TL out put amongst the choosen concentration. Thus optimum conc. of Bi in the host seems to be around 0.1% and for Tb it is around 0.005% .

B) Activation Energy

The activation energy 'E' of a glow peak can be evaluated by several ways as described in section 4.3. In the present study activation energies are calculated from the shpae of glow curve by using method due to -

i) Urbach (ii) Luschik (iii) Halperin & Branner, (iv) Chen (v) Grossweiner, values thus calculated by different formulae are listed in table no. 4.2 and are in good arrangement for the CaS:Mn:Dy and CaS: Bi: Tb phosphor.

c) Variation of activation energy with activator concentration -

From Table no. 4.2, it is observed that activation energy does not vary significantly with activator concentration. The effective trap levels are distributed from 0.44eV to 1.2 eV. for CaS:Bi:Tb and 0.5 to 1.7 eV for CaS:Mn:dy, observed variation is not systematic with respect to concentration variation. This suggests that the addition of activators does not introduce any new traps but only modifies the relative importance of traps responsible for thermoluminescnece, (23, 24).

d) Kinetics of Luminescnece

Kinetics of luminescence can be determined by various methods. The symmetry factor $\mu g = \delta / w$, is a characteristic of the type of kinetics involved in the process. The values of symmetry factor are listed in table no. 4.2

In the present study the values of μg for some samples the values are less than $e^{-1}(1+ 2/\Delta)$ and for others, the values are greater. This may be due to the composite nature of the glow peak instead of a single peak.

For CaS:Bi:Tb the variation in the μg (symmetry factor) is systematic and which is not for CaS:Mn:Dy. But both the phosphors having μg values less and greater than $e^{-1}(1 + \frac{2}{\Delta})$. Hence any conclusion about the kinetics, drawn from the magnitude of μg is likely to be erroneous. Efforts are therefore made to determine kinetics by another method.

e) Escape frequency factor - The escape factor 's' calculated by using eqn. (4.8) with different values of activation energies obtained from different methods given in section 4.3.3. The escape frequency factor is dependent on E. The 's' values are calculated by taking E values from Halperin and Branner and Grossweinner formula. They are listed in table no. 4.3 for both the phosphors. The 's' values vary from 10^2 to 10^8 sec^{-1} for CaS:Bi:Tb and 10^3 to 10^9 sec^{-1} for CaS:Mn:Dy phosphor.

f) Size of traps :

The size of trap can be evaluated from the knowledge of escape frequency factor. The values of σ are calculated by using equation 4.6.4. The values are listed in table no.4.3. The size of the trap is about 10^{-17} to 10^{-23} cm^2 for CaS:Mn:Dy and that for CaS:Bi:Tb 10^{-17} to 10^{-23} cm^2. This trap size in the present work is of medium size trap (29.)

g) Dose dependance

The excitation dose will affect the peak intensity, of the glow curve, Intensity is function of excitation dose. The glow curves for various excitation time are shown in fig. 4.11 for a sampel MD 24. The peak intensity of glow curve initially increases gradually and then it saturates around 45 minutes.

Table No. 4.1:- Observation Table showing the peak temperature and peak intensity values obtained from glow curves of uv excited sample.

Sample No.	Peak temp °k	Peak intensity nA.
MD-18	613	279
MD-19	613	199
MD-20	613	199
MD-21	613	149
MD-22	613	319
MD-23	613	349
MD-24	613	389
MD-25	613	279
MD-34	613	137
MD-35	593	167
MD-26	613	149
MD-27	613	235
MD-28	613	219
MD-29	633	175
MD-30	593	127
MD-31	613	149
MD-32	613	209
MD-33	633	395
MD-36	613	119
MD- 37	613	159

Table No.4.2 : showing activation energy calculated with different formulae (uv-excited samples).

Eu - Energy calculated from Urbach formula
ELC - Energy calculated from Luschik formula with Chen's correction.

E_{HBC}- Energy calculated from Halperin & Branner formula with Chens correction.

E_C - Energy calculated from Chen's formula

E_{GC}- Energy calculated from Grosswiener formula with Chen's correction.

Sample no.	Ec eV	E_{LC} ev	E_{GC} ev	Eu ev	E_{HBC} ev	μ
ID.18	0.7383	1.1031	0.5243	1.226	0.6275	0.3541
ID.19	0.6587	1.1058	0.4967	1.226	0.4487	0.2452
ID.20	0.7045	1.1058	0.5783	1.226	0.5367	0.3
ID.21	0.8364	1.1072	0.6395	1.226	0.6027	0.2558
ID.22	1.0325	0.9962	1.1487	1.226	1.12395	0.56
ID.23	0.9482	1.1651	1.0949	1.226	1.0659	0.5740
ID.24	0.9892	1.1044	0.9640	1.226	0.9526	0.4054
ID.25	1.1052	1.1755	0.9583	1.226	0.9185	0.4468
ID.34	0.5403	0.9928	0.5218	1.186	0.4787	0.3898
ID.35	1.10813	1.1653	0.71189	1.186	0.9409	0.4545
ID.26	1.2178	1.2020	1.2734	1.226	1.2575	0.5348
ID.27	0.9708	1.2973	0.8254	1.226	0.8003	0.325
ID.28	1.3919	1.3823	1.4237	1.226	1.5289	0.5263
ID.29	0.9194	1.6865	0.6844	1.226	0.6483	0.2380
ID.30	0.8484	0.7839	1.02176	1.186	0.9908	0.5892
ID.31	0.8588	1.1297	0.7415	1.226	0.7126	0.3333
ID.32	1.518	1.0544	1.0679	1.226	1.0645	0.4285
ID.33	0.9448	1.1243	0.86011	1.226	0.8377	0.3658
ID.36	0.8428	0.9873	0.7619	1.226	0.7066	0.4666
ID.37	0.7210	0.9885	0.6178	1.226	0.5794	0.3265

Table No.4.3 : Showing frequency factor and size of trap (uv.excitation).

Sample no.	Frequency factor S_{EGC}; sec^{-1}	S_{EHBC}, sec^{-1}	Size of trap σ cm^2
MD.18	7.4332×10^{2}	6.27010×10^{3}	4.1800×10^{-23}
MD.19	4.1798×10^{2}	1.5244×10^{2}	1.0163×10^{-24}
MD.20	2.2782×10^{3}	9.6263×10^{2}	6.4174×10^{-24}
MD.21	8.0165×10^{3}	3.7652×10^{3}	2.5100×10^{-23}
MD.22	2.1916×10^{8}	1.3440×10^{8}	8.9606×10^{-17}
MD.23	7.5747×10^{7}	4.2509×10^{7}	2.8339×10^{-19}
MD.24	5.6007×10^{6}	4.4522×10^{6}	2.9681×10^{-20}
MD.25	4.9917×10^{6}	2.2550×10^{6}	1.5034×10^{-20}
MD.34	1.0538×10^{3}	4.1562×10^{2}	2.7707×10^{-24}
MD.35	5.9079×10^{4}	6.8849×10^{6}	4.5899×10^{-20}
MD.26	2.5714×10^{9}	1.8802×10^{9}	1.2534×10^{-17}
MD.27	1.9948×10^{5}	1.2201×10^{5}	8.1341×10^{-20}
MD.28	4.9294×10^{6}	3.8807×10^{7}	2.5871×10^{-19}
MD.29	1.2500×10^{4}	6.1079×10^{3}	4.07196×10^{-23}
MD.30	3.6266×10^{7}	1.9198×10^{7}	1.27985×10^{-19}
MD.31	6.400×10^{4}	3.5628×10^{4}	2.3752×10^{-22}
MD.32	4.4239×10^{7}	4.1351×10^{7}	2.7567×10^{-19}
MD. 33	3.9254×10^{5}	2.5346×10^{5}	1.6897×10^{-21}
MD.36	9.6824×10^{4}	3.1545×10^{4}	2.1030×10^{-22}
MD.37	5.1437×10^{3}	2.3285×10^{3}	1.5523×10^{-23}

S_{EGC} - Escape frequency factor calculated by taking activation energy E_{GC}.

S_{EHBC} - Escape frequency factor calculated by taking activation energy E_{HBC}.

σ - size of the trap calculated by taking, E_{HBC}.

References

1. Armu, F. and Maxia, V.J. Luminescance, 10, 77 (1975)

2. Braunlich, P. Thermoluminescnece and thermally stimulated current tools for the determination of trapping parameter. Thermoluminescence of Geological material Ed. by D.J. McDougall (Academic Press).London and New York, P 61 (1964)

3. Braunlich, P. comments on the optical rise method for determining trap depth, J.Appl. Phys, 38, 2516 (1967).

4. Booth, A.H. Canad, J.Chem, 32, 214, (1954).

5. Bonun A., Czech, J.Phys. 4, 91 (1954).

6. Chen, R. J.Electrochem, Soc. 116, 1254. (1969)

7. Chen. R., and Winer, S.J.Appl. Phys. 41, 5227 (1970)

8. Chemmy, P.J.Townsend P.D. and Levy P.W., Phys. Rev. 155, 917 (1967).

9. Curie, D. "Luminescence in Crystals" (Methuen Lond), 162(1963).

10 Dussel, G.A. and Bube, R.H. Phys. Rev. 155, 764 (1967).

11. Dhayagude N.S., Ph.D.Thesis, Shivaji University, Kolhapur (1984)

12 F.Urbach, Akad wiss Wien Ber. 139, 20, 354 (1930)

13 Garlick, G.R.J. and Gibson, A.F. Proc. Roy. Soc. (London), A. 60, 574 (1948).

14 Gross Weiner, L.J.J.Appl.Phys. 24, 1306 (1953).

15 Garlick, G.F.J. "Luminescence Material" (Oxford Univ. Press, New York) (1949).

16 Halperin, A. and Braner, A.A., Phys.Rev. 117, 408 (1960)

17 Halperin A, Braner A.A., Ben Zvi, A. and Kristianpoller, N.Phys, Rev. 117, 416 (1960)

18 Hoogenstraaten, W., Philips Res. Rep. 13, 515 (1958).

19 Kelly P and Braunlich P. "Phenomendogical theory of thermoluminescence" Phys. Rev. 131, 1587 (1970)

20 Luschik, Ch. B. Dok; Acad. Nauk S.S.S.R. 101, 641 (1955).

21 Lawangar R.D., Shalgaokar C.S., Pawar S.H. and Narlikar A.V. Solid State Commun. 10, 124 (1972).

22 Lawangar,R.D.,Ph.D., Thesis, Shivaji Univ. Kolhapur, (1974)

23 Sinha, O.P. and Shrivaraman, S. Indian J.Pure Appl. Phys. 10, 134 (1972).

24 Lawangar R.D. and Naralikar A.V., J. Luminescence 11, 135.(1975).

25 Murti, Y.V. and Murthy K.R.N.Thermoluminescence of Cu activated NaCl crystal J.Phy. Chem (sol. St. Phy.) S. 2827 (1972).

26 Mott N.F. and Gurney R.W. Electronic Processes in Ionic Crystal, (Oxford Clarendon), 108 (1948).

27 N.F.Mott and R.W.Gumey, "Electronic Process in Ionic Crystals", Ed. By D.J.McDougoli (1968)

28 Nambi K.S.V. Bapat, V.N. and Ganguly A.K. J. Phys. C. 7, 103 (1974).

29 Patil M.G., Ph.D.Thesis,Shivaji University, Kolhapur (1981).

30 Parfianovitch, J.A., J.Exp. Theor. Phys. S.S.R., 26, 696 (1954).

31 Randall and Wilkins Proc. Roy. Soc. A.184, 366 (1945).

32 R.Chen, J.Appl. Phys. 54, 570(1969).

33 Shenkar D and Chen.R. Numerical solution of the glow curve differential equation J.Comptation Phys. 10, 272 (1972).

34 Schon, M.Tech, Wiss, Abh. Osran, Ges, 7, 175 (1958).

35 Jain S.K. and Sinha O.P.Indian J. of Phys. 48, 1100(1974).

36 Sunta C.M.NuCl Tracks, vol. 10, Nos. 1/2 pp. 47-53, (1985).

37 Urbach, F. Cornell symposium (Wiley New York), 115, (1946)

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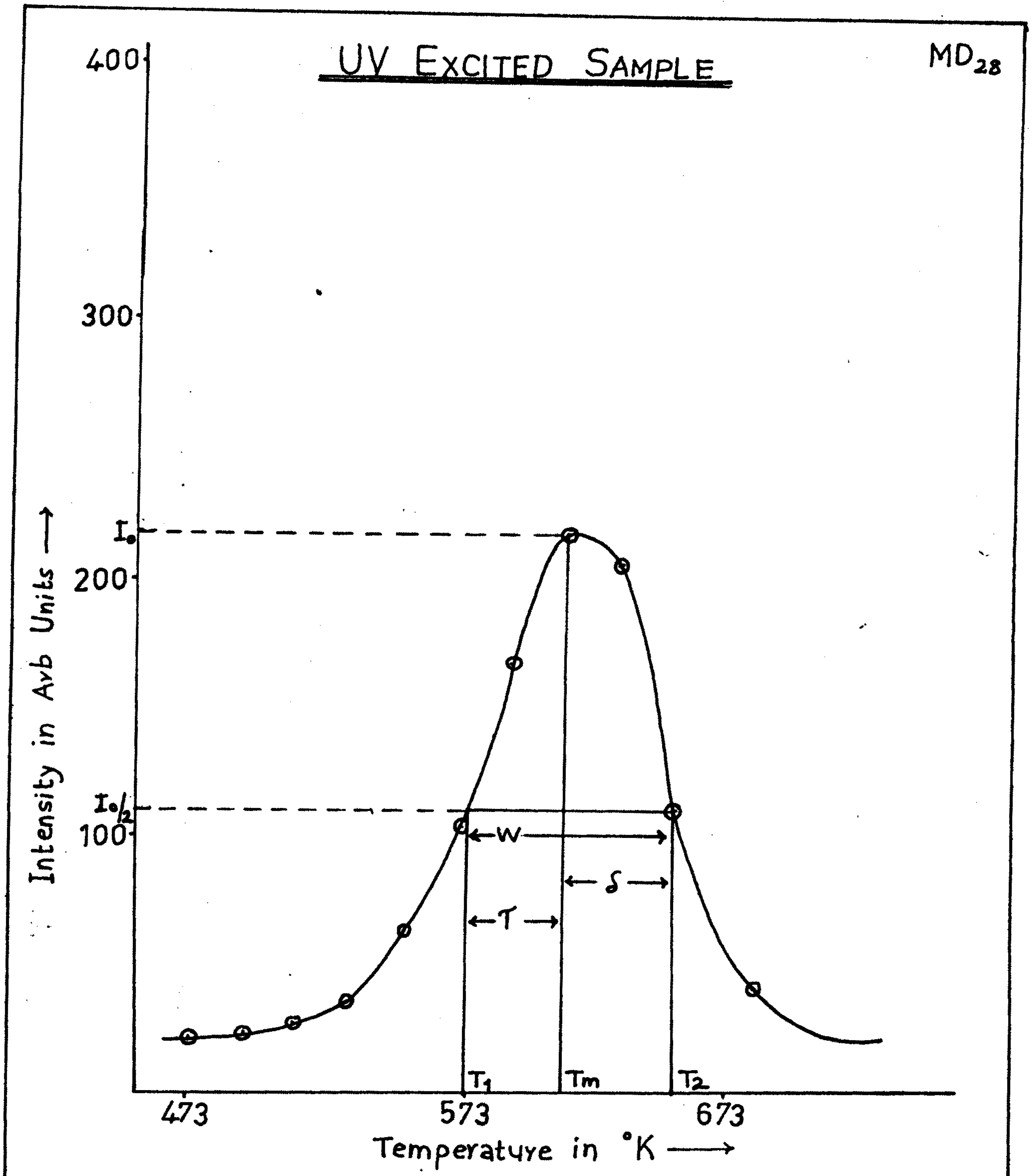
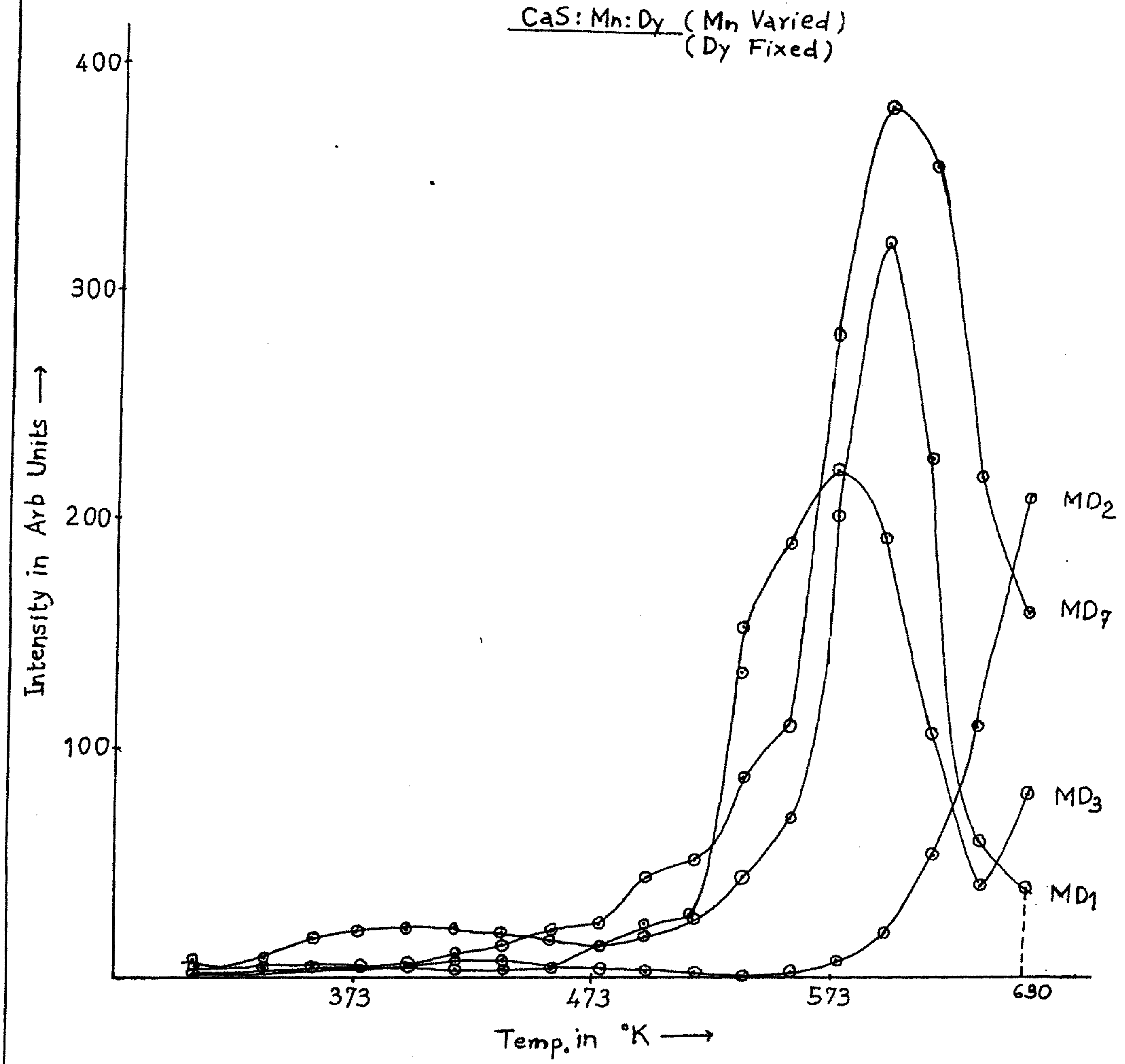


UV EXCITED SAMPLE

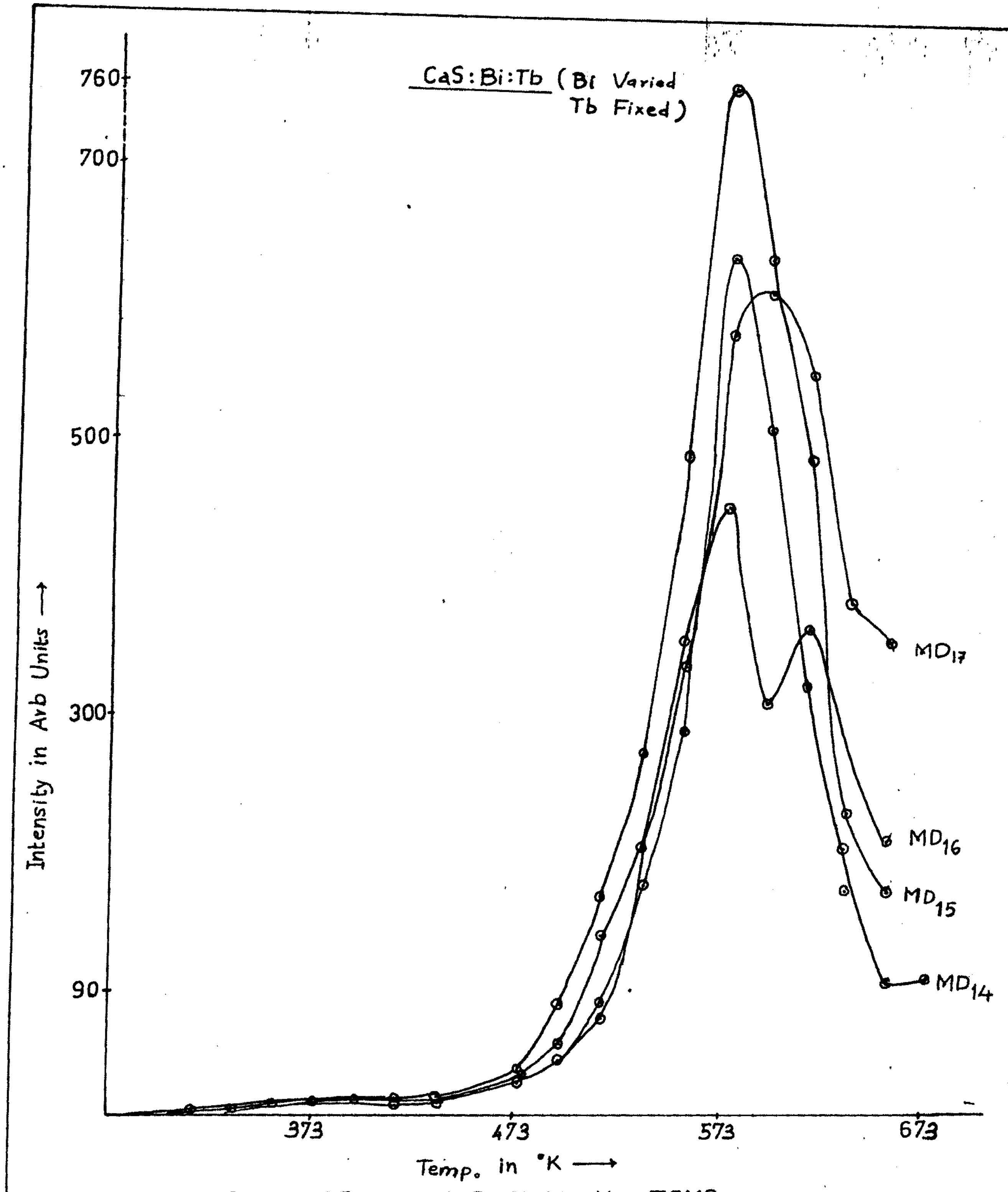
TYPICAL GLOW CURVES FOR CaS : Mn : Dy PHOSPHORS

FIG. NO.: 4.1.



PLOTS OF TL INTENSITY Vs TEMP.

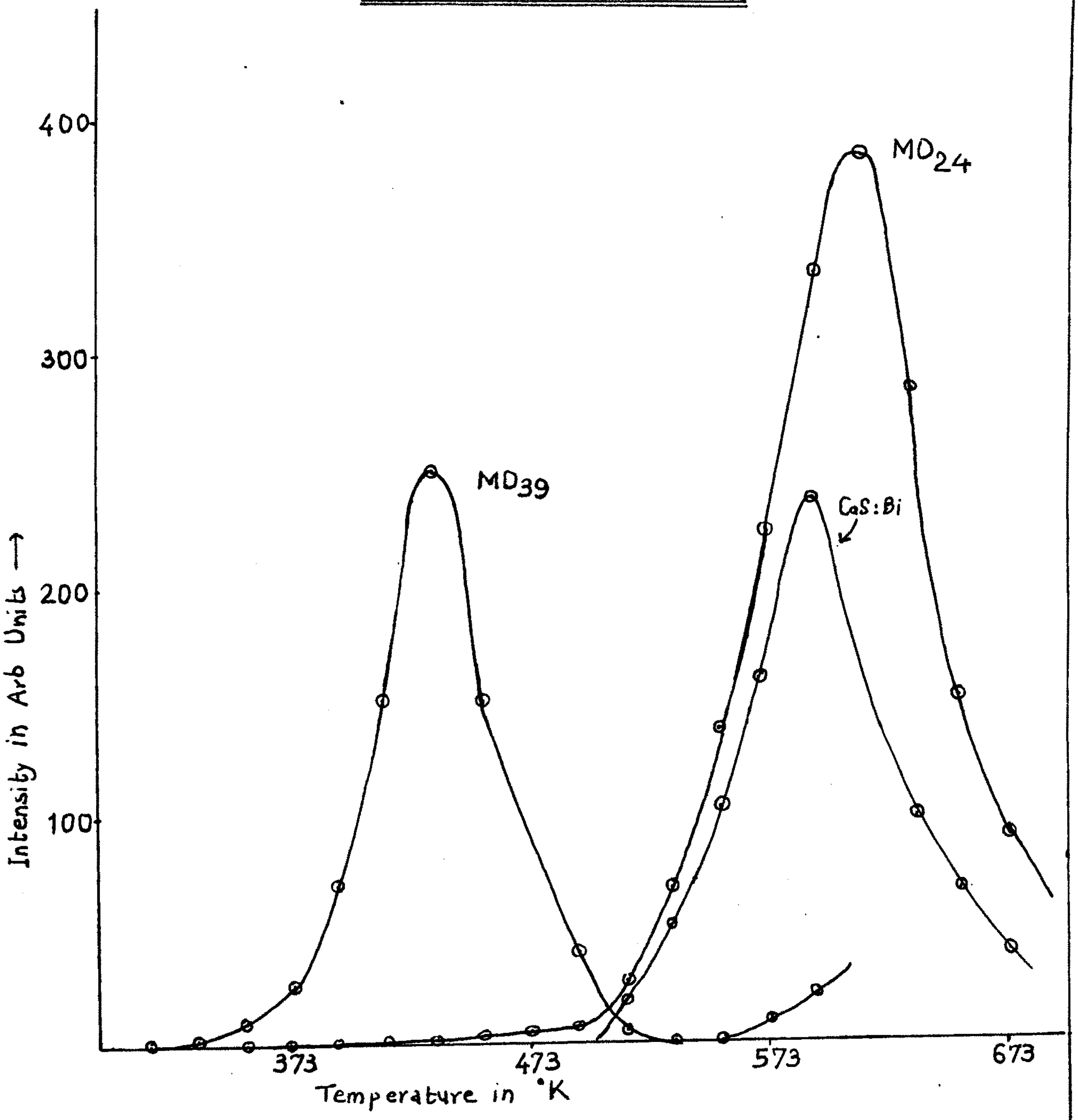
FIG. NO.: 4.2



PLOTS OF TL INTENSITY Vs TEMP.

FIG.NO.:4·3.

UV EXCITED SAMPLES



GLOW CURVES FOR CaS:Bi:Tb (MD24) AND CaS (Undoped) Phosphors.

FIG. NO.: 4·4.

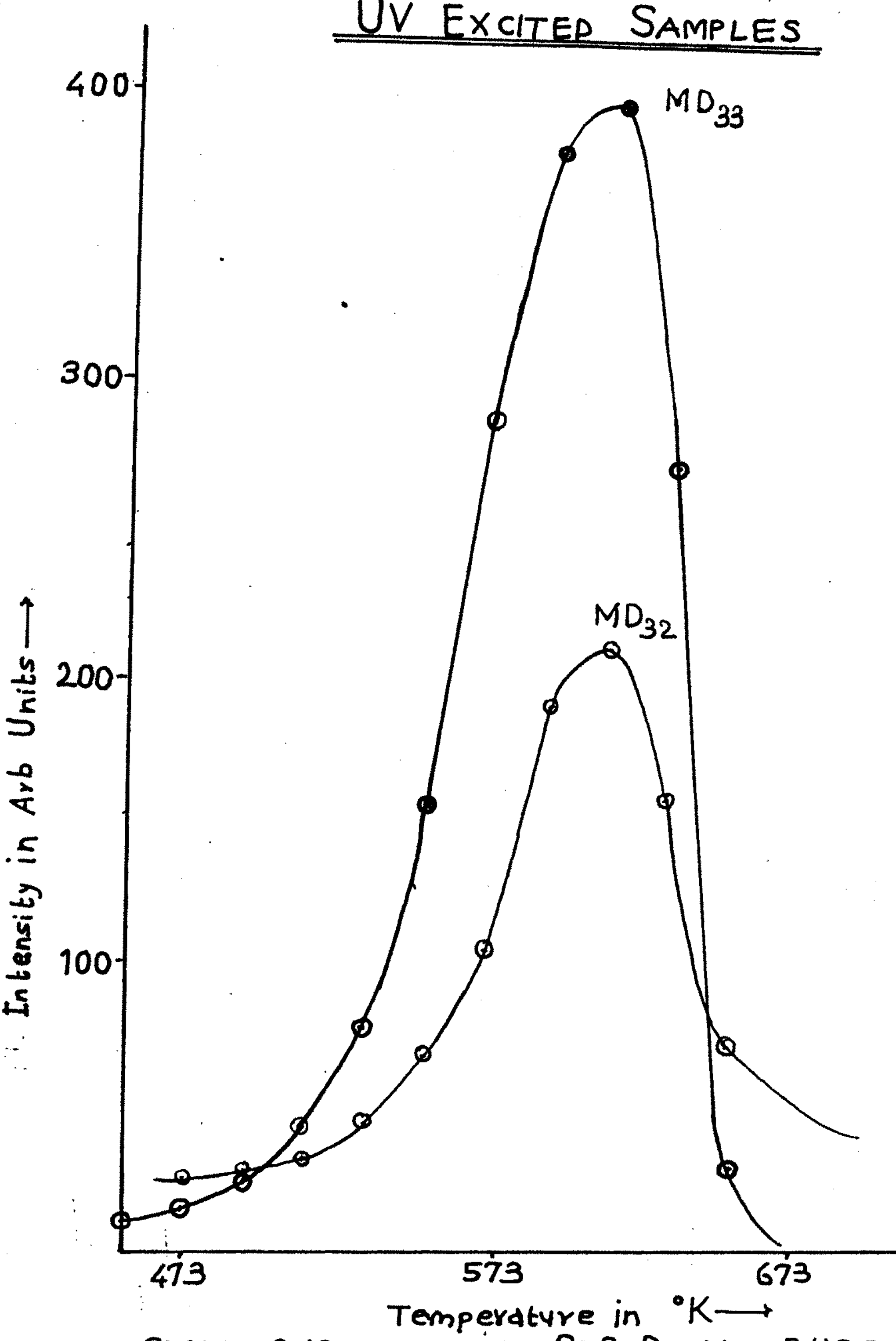
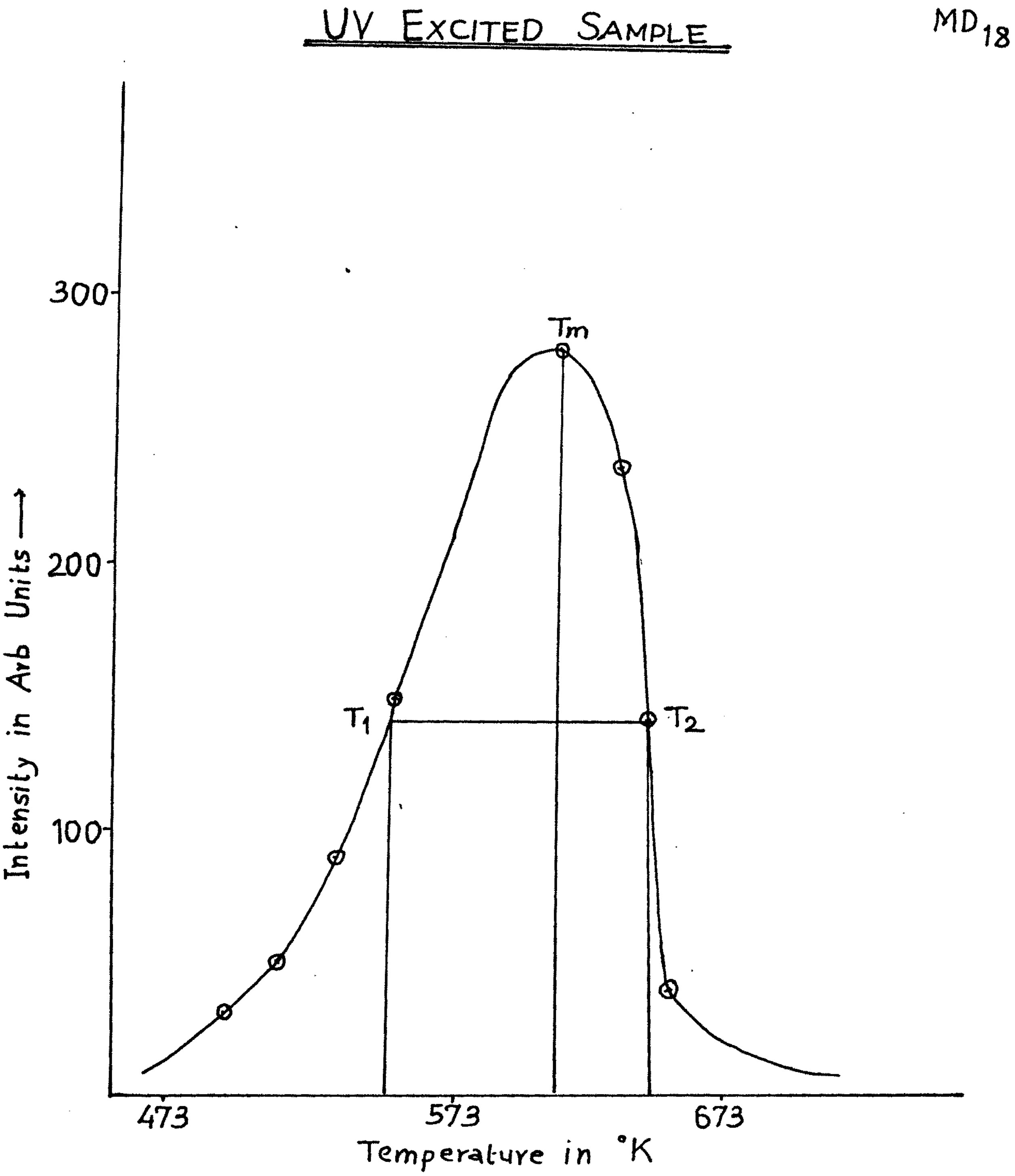


FIG. NO.: 4.5.

GLOW CURVES FOR CaS: Dy: Mn PHOSPHORS



TYPICAL GLOW CURVES FOR CaS : Bi : Tb PHOSPHORS

FIG. NO. : 4.6

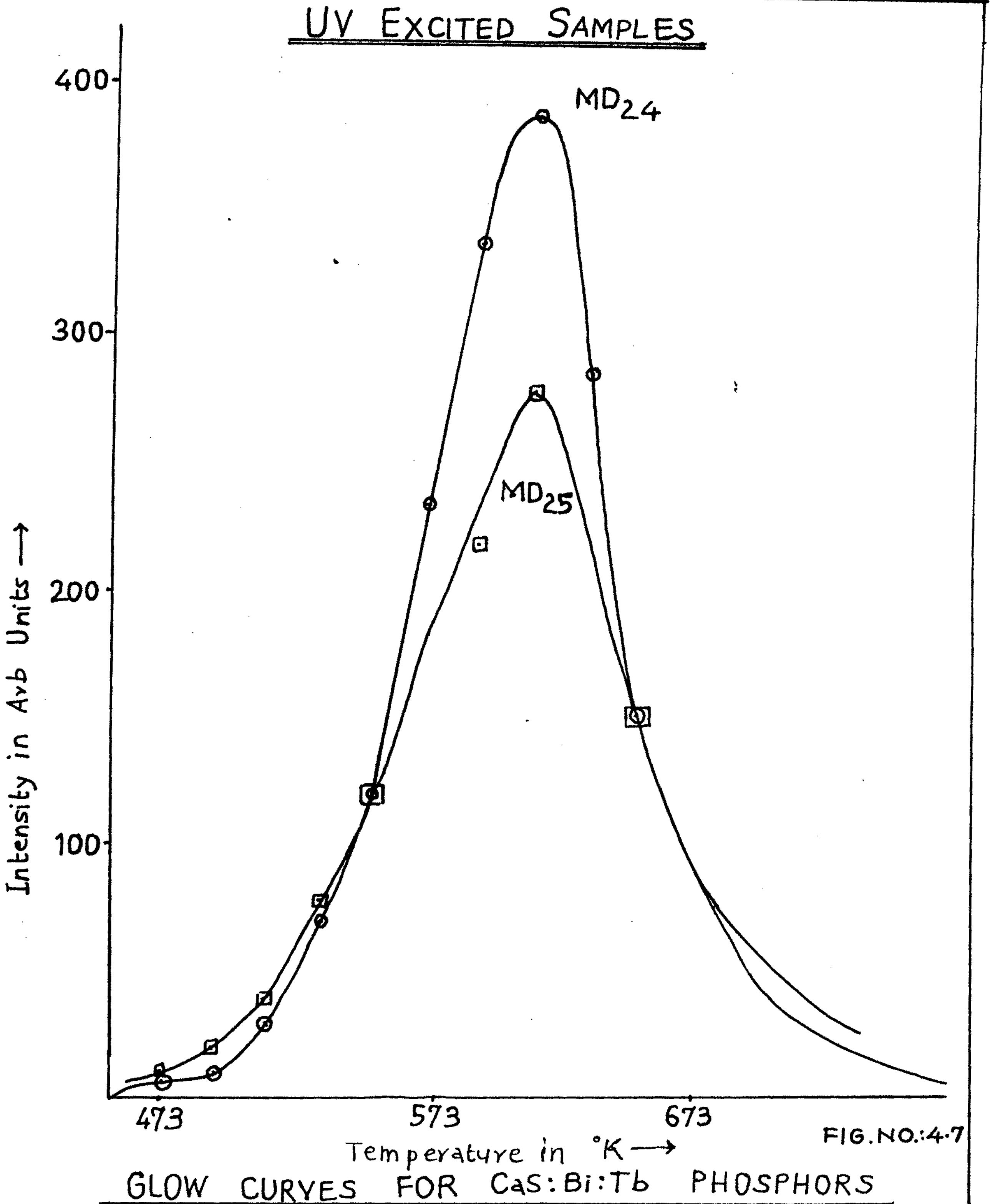


FIG. NO.: 4·7

GLOW CURVES FOR CaS:Bi:Tb PHOSPHORS

VARIATION OF PEAK INTENSITY WITH CONCENTRATION.
(UV EXITED SAMPLES)

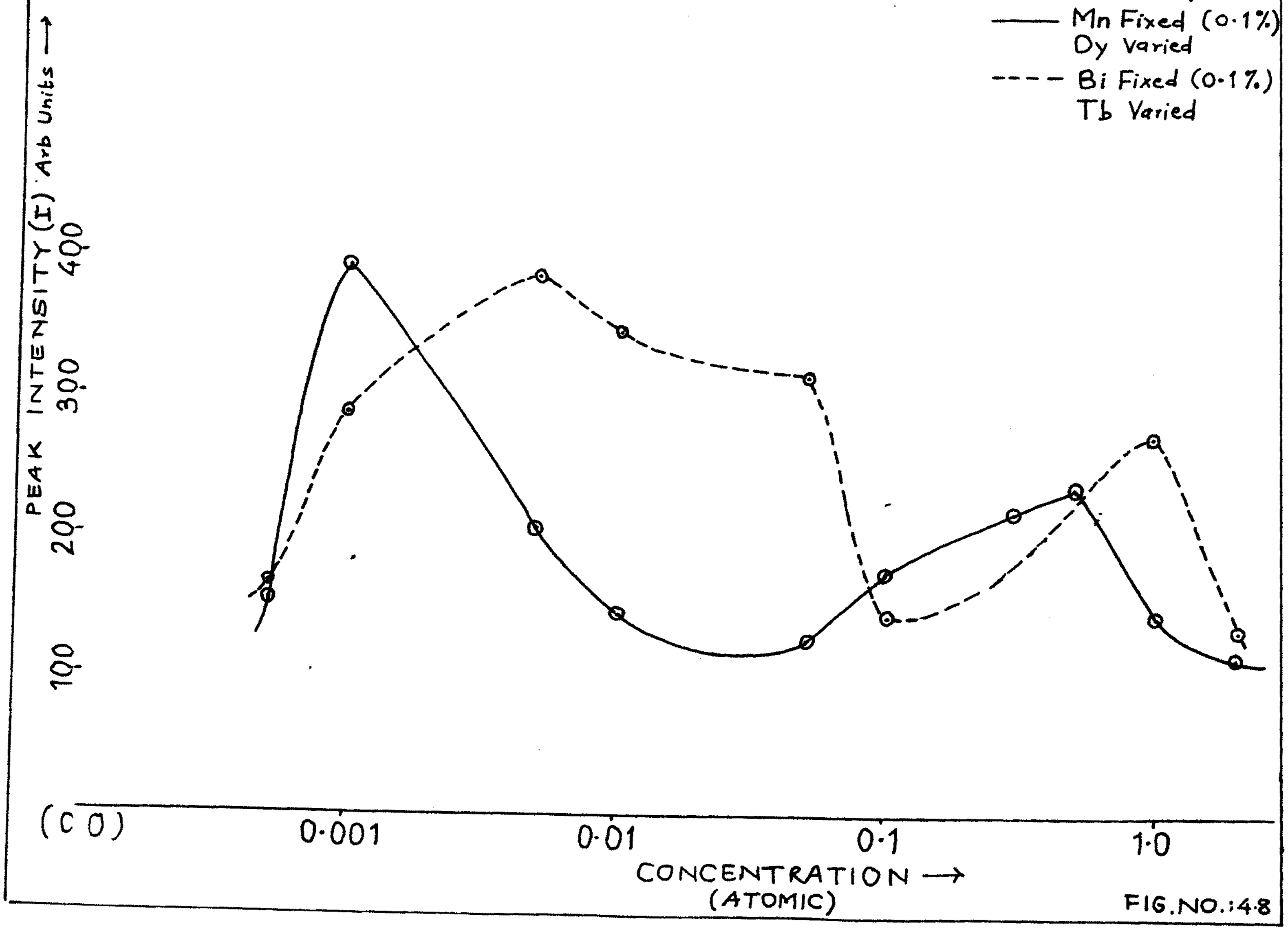
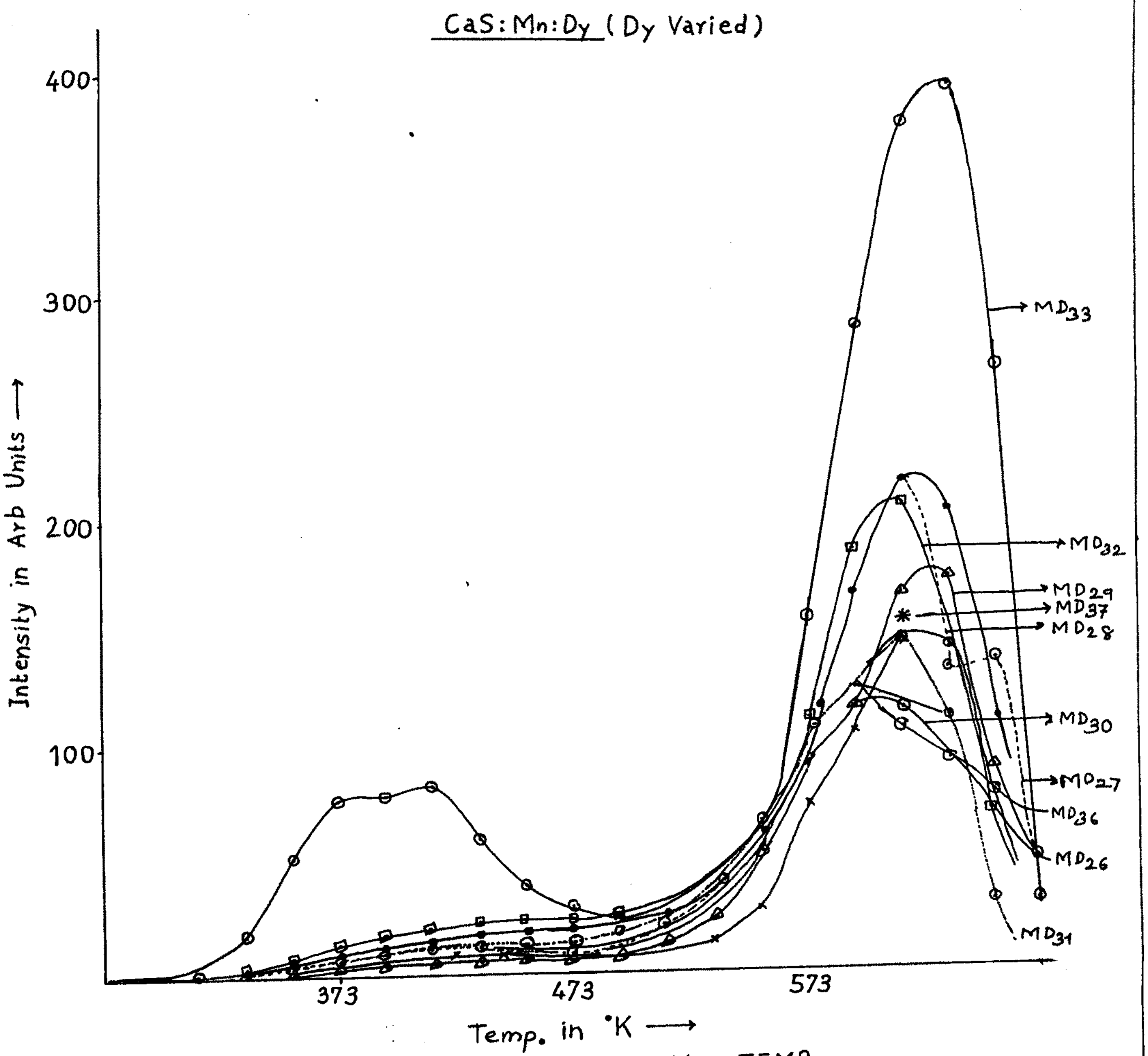


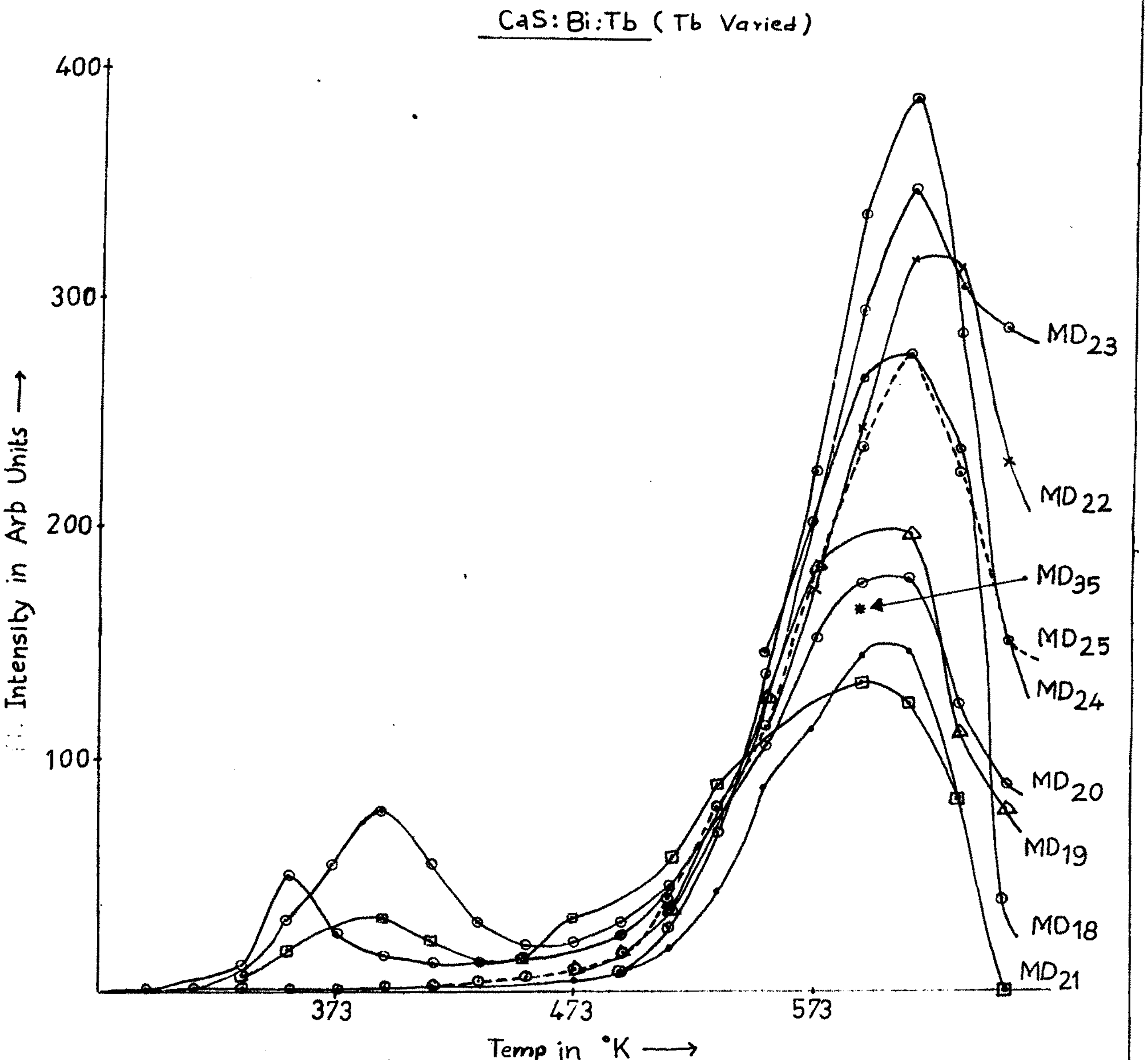
FIG.NO.:4·8



CaS:Mn:Dy (Dy Varied)

PLOTS OF TL INTENSITY Vs TEMP.

FIG. NO.: 4.9.



PLOTS OF TL INTENSITY Vs TEMP.

FIG. No.: 4.10

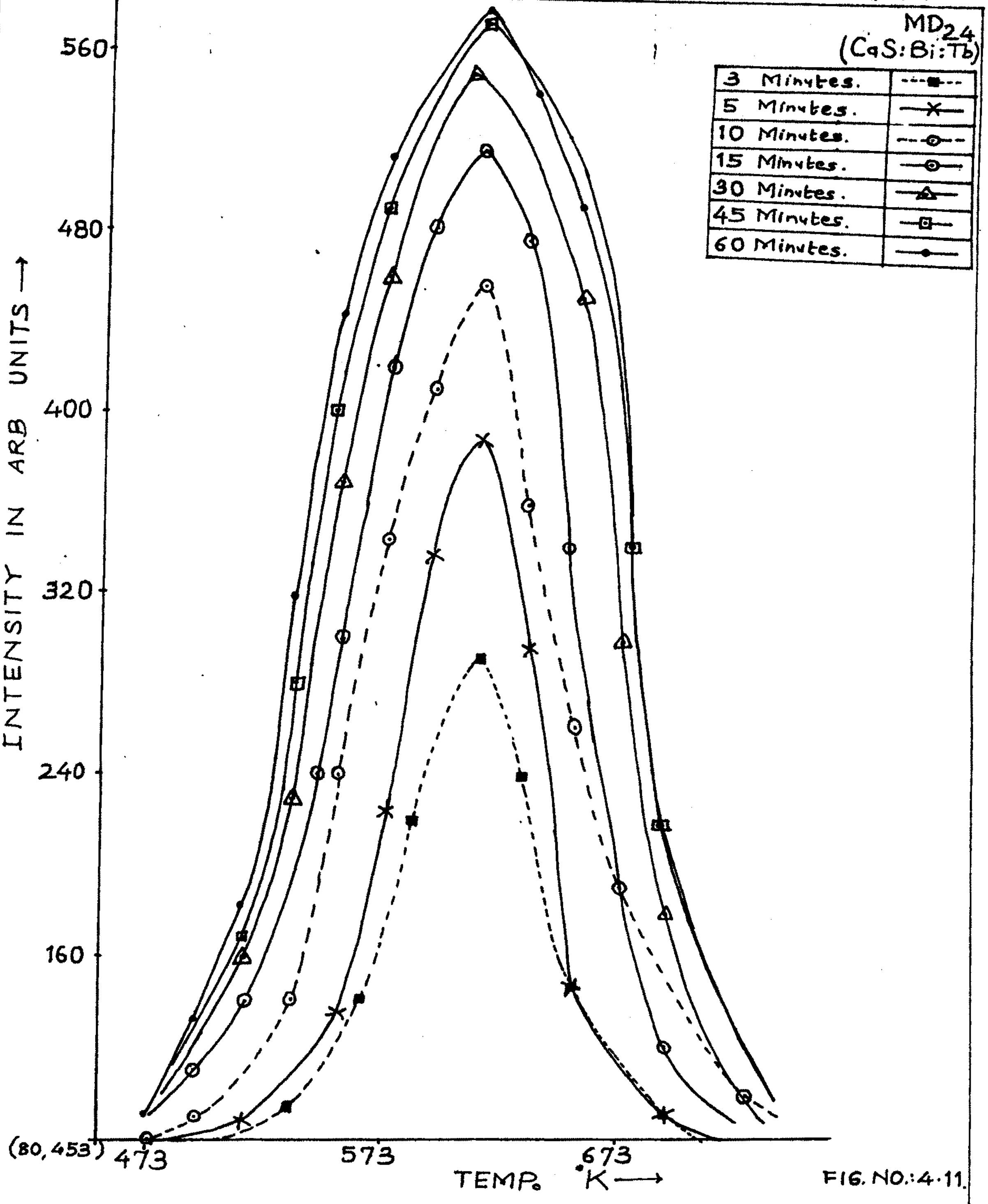
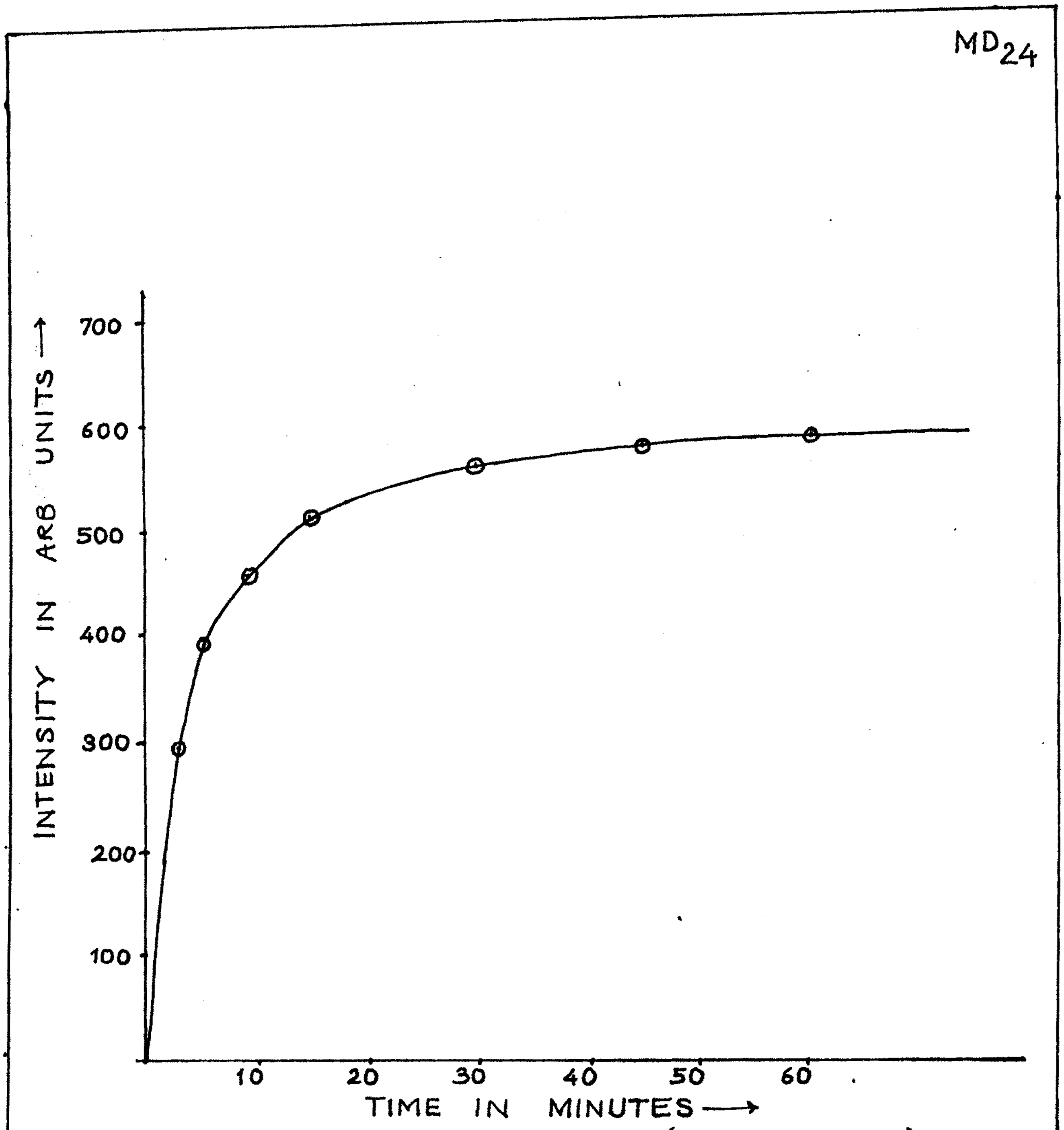


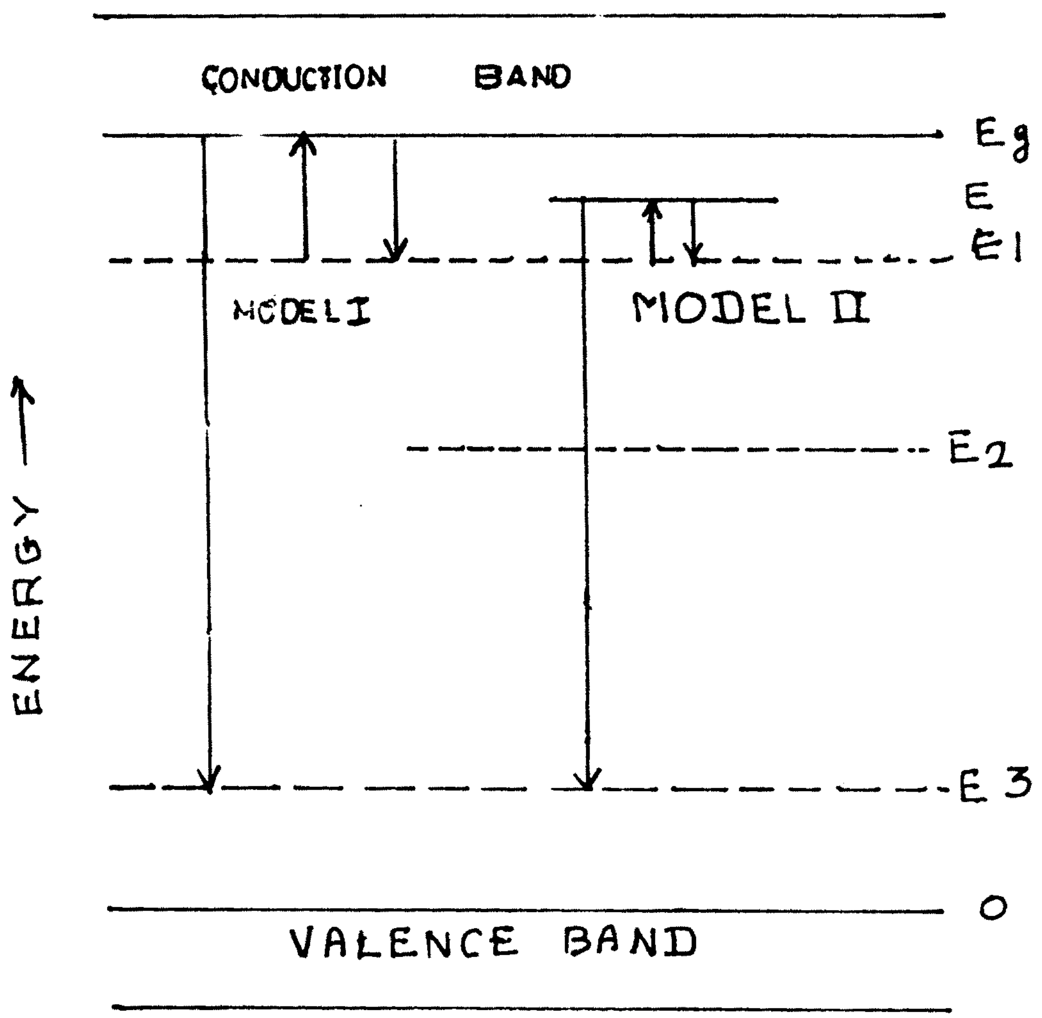
FIG. NO.: 4·11.

TL GLOW CURVES OF PHOSPHORS FOR DIFFERENT TIME OF EXCITATION.



DOSE DEPENDANCE (UV EXCITATION)

FIG. NO.: 4·12.



ENERGY BAND MODEL OF THERMOLUMIN.
THERMOLUMINESCENCE

FIG. NO.: 4.13