CHAPTER IV

THERMOLUMINESCENCE

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4.1 INTRODUCTION

Thermoluminescence (TL) is the phenomenon in which substance (phosphor) emits light, when previously excited sample (either by uv or x-ray or gamma ray) is heated. In this case temperature is not the exciting agency, but a stimulant. Phosphorescence at any temperature is emission of light after exciting agent is removed. The intensity of the luminescent emission is measured as a function of temperature. The pattern of resultant light out-put versus temperature is called TL glow curve. TL glow curve may exhibit many peaks depending upon the number of traps involved i.e. on the nature of the material.

Significance of Peaks

When the material is excited by any kind of irradiation equal number of electrons (or holes) are liberated within it. Some of these are trapped at certain centres called as electron(or hole)traps, which stores the energy. Therefore, these traps are referred as 'storage centres'.These electrons (or holes) can be liberated by thermal stimulation.

For such materials of different trap depths, detrapping is also possible at different temperatures, resulting in 'bursts' of light recorded as 'glow peaks' in TL glow curve.

The number of peaks in the glow curve indicates, the different luminescent centres or different metastable states of the same centres.

The TL glow curves can be used, to determine activation energy (E), escape frequency factor(s), and size of the trap. TL glow curve gives valuable information about the role of different impurities in the host.

In the present investigation, TL glow curves of $CaSO_4$ doped with different percentages of concentrations of Mn and rare earths are studied to obtain the following information :-

1] To find suitable co-acitavtor.(second . rare earth activator)

2] Regarding optimum concentrations of Mn and RE in the host for maximum TL output.

3] The effect of activator concentration on shape of glow curve and trap distribution.

4] Nature of distribution of trapping levels.

5] Estimation of escape frequency factor.

6] Determination of size of traps.

7] The kinetics involved in the TL process.

8] Comparative status of the general shape of glow curves, and of activation energy under different irradiations.

9] Dose depedance of TL glow peaks, under uv and gamma irradiation.

4.2 THEORY OF GLOW CURVE

4.2.1 TL GLOW CURVE PARAMETERS

The simplest and commonly used technique for studying the TL glow curve is the one suggested by Urbach(1) and Randall and Wilkins(2) for the calculation of TL intensity. It is presumed that, the trapped electrons have Maxwellian distribution of thermal energies and the probability 'p' for the thermal release of trapped electron from the trap per unit time is given by -

$$P = se^{-E/KT} \quad \text{..} \quad (4.1)$$

so that, TL intensity is given by

$$I_t \propto n_t \cdot p \quad \text{..} \quad (4.2)$$

where T = absolute temperature.

K = Boltzman constant.

E = trap depth or activation energy.

S = constant, having the dimensions of frequency called as escape frequency factor.

n_t = 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 the trap given by,

$$S = V_c N_c S_T \qquad .. \qquad (4.4)$$

where V_c = thermal velocity of electron in conduction band.

N_c = density of available trap levels.

In the 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 walls and the wall reflection coefficient. It then follows that, the values of 's' should be of the order of or less than the vibrational frequency of the crystal (3). However, in practice one does come across situation where 's' takes values differing from lattice phonon frequencies by many order of magnitude. This is attributed to fluctuation in local environement of the trap such as produced by a nearby impurity, causing change in the frequency of localised phonons.

4.2.2 RANDALL AND WILKINS THEORY (FIRST ORDER KINETICS)

Randall and Wilkins (2) have given, a simplest mathematical representation for the luminescence glow peaks without any overlaping The basic assumptions are made as -

i] An injection of electron is the only rate determine 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 heating, if 'n' is the concentration of filled traps at any time 't'(temp.T) then the intensity of TL is given by

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

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

$$= -c\ Pn$$

$$\therefore I = -cnse^{(-E/KT)} \qquad .. \qquad (4.5)$$

where 'n' is number of trapped charge carriers (electrons and holes) and 'C' is a constant.

$$\therefore \frac{dn}{n} = -Cse^{-E/KT} \cdot \frac{dt}{dT} .dT$$

$$\therefore \quad = -C \frac{S}{\beta} e^{-E/KT} . dT \qquad .. \qquad (4.6)$$

where $\beta = \frac{dT}{dt}$

by integrating and substituting in equation, the TL intensity turns out to be,

$$I = n_0 Cse^{-E/KT} \quad \exp\left[-\int_0^T \frac{S}{\beta} e^{-E/KT'} \cdot dT'\right] \qquad (4.7)$$

where 'n_0' 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 $T = T_m$, and then falls off for further increase in temperature.

By setting $dI/dT = 0$ at $T = T_m$, one obtains the important relationship,

$$\frac{\beta E}{K T_m^2} = s e^{-E/KT_m} \quad .. \quad (4.8)$$

At a fixed temprature T, $c\,s\,e^{(-E/KT)}$ is a constant, say A. Equation (4.5) can thus be written as,

$\frac{dn}{n} = -dt$ which on integration gives,

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

from equation (4.5) and (4.8)

$$I = I_o \cdot e^{-AT} \text{ where } I_o = An_o \quad .. \quad (4.10)$$

Thus, when at a fixed temperature 'T' the TL intensity decays expoentially, the TL process is said to be following the first order Kinetics.

4.2.3 GARLICK AND GIBSON THEORY (SECOND ORDER KINETICS)

Garlick and Gibson(4) extended the Randall & 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 relased carrier will go to the recombination centre is

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

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

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

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

$$I = \frac{n_o^2 \cdot cse^{-E/KT}}{\left[1 + s' \frac{n_o}{\beta} \int_0^T e^{(-E/KT')} dT'\right]^2} \quad \ldots\ldots \quad (4.12)$$

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

At a fixed temperature 'T', equatin for TL intensity can be derived as -

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

where $A' = Cs'e^{-E/KT}$

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(5,6)

Fig. (4.1) shows 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 and E_2 with electrons, while E_3 traps holes from the valence band. The thermal depopulation of shallow trap at E_1 with deeper traps 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 levels E_1

N_2 = concentration of traps at energy levels E_2

N_3 = concentration of traps at energy levels E_3

n_1 = concentration of electrons in traps at E_1
n_2 = concentration of electrons at traps E_2
n_c = concentration of electrons in the conduction band.

n_v = conentration of holes in the valene band (assumed to be zero)

P = Probability per second of the eletron release from the traps E_1 , given by

P = $se^{(-E/KT)}$ where E is trap depth of level E

E = $E_g - E_1$ for model I

E = E' - E, for model II

q is retrapping coefficient, R = recombination coefficient as introdued in following rate equation model I see (fig.4.1)

The rates at which the concentration of trapped electrons and conduction eletrons vary are given by

$$\dot{n}_1 = -pn_1 + q\, n_c\, (N - n_1) \quad .. \quad (4.14)$$

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

The charge balance gives,

$$N_3 = n_1 + n_2 + n_c \quad .. \quad (4.16)$$

The differential equations are analytically untraceable without the following simplifying assumptions

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

Justification of these assumptions is to be found in the work of Kelly et al.(6) and Shenkar and Chen(7) who obtained numerical solutions of the equation, to check the assumptions with these assumptions the rate equations are readily integrated to yield the density of trapped electron as a functin of temperature. When linear heating program $\beta = t$ is used.

$$\left(1 - \frac{f N_1}{N_2}\right) \ln X - F\left(1 + \frac{N_1}{N_2}\right) \ln \frac{n_1 + N_2}{n_o + N_2} + \int_{T_o}^{T} \frac{S}{\beta}\, e^{-E/KT'} .\, dT' = 0 \qquad .. \quad (4.18)$$

which reduces, when N_2 is negligible

$$(1 - f) \ln x + \frac{f}{Y}\left(1 - \frac{1}{x}\right) + \frac{S}{\beta} \int_{T_o}^{T} e^{-E/KT'} .\, dT' = 0 \qquad ..(4.19)$$

where $x = \frac{n_1}{n_o}$, $y = \frac{n_o}{N_1}$; $f = \frac{q}{R}$

'n_o' being the density of electrons on traps 'E' at the initial temp. 'T' the thermoluminescence intensity, 'I', for model 1 - I given by

$$I_1 = \frac{P(n_1^2 - n_1 N_2)}{N_2 + fN_1 - (1 - f)\, n,} \qquad .. \quad (4.20)$$

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 reduced to first order and second order cases when f = 0 and f = 1 resp.

Model II - The trapped electrons are taken to the excited state 'E' from which they tunnel to recombination centre (The rate equation given by Murti(9)) .The theoretical glow curve for this model can be obtained from the following two equations :

$$\left(1 + \frac{S}{fN_2}\right) \ln x - \frac{S}{fN_2} . \ln \frac{n_1 + N_2}{n_o + N_2} + \int_{T_o}^{T} . \frac{P}{\beta}\, dT' = 0 \quad (4.21)$$

and

$$I_2 = \frac{P . n_1^2}{n_1 + \frac{S}{\beta f}} \qquad .. \quad (4.22)$$

while applying model I of the above approach to determine the TL parameters, Braunlich(8) and Shenkar and Chen (7) showed the dependane of the obtained values on the trap occupancy Shenkar and Chen in particular demonstrated by computation that the term 'Kinetics Order' may beome meaning less, if the inequality

$RN_3 > q(N_1 - n_1)$ or

$RN_3 < q(N_1 - n_1)$

changes direction during the TL glow peak emission.

4.3 METHODS FOR DETERMINING TRAP DEPTHS

There exist several methods for determination of trap depth from glow curves. In this section, methods 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. 4.2 represents a general shape of glow curve defining some characteristic quantities such as T_m, T_1, T_2, δ, w etc. It can be approximated by a triangle. This principle has been used for the derivation of several expression for the trap depth.

a) Method using high temperature side of the glow peak (after Luschik(10))

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 that of luminescene centres. Byassuming that the area of the half peak towards the fall off is equal to the area of the triangle having the same height and half width, Luschik(10) showed that the activation energy for the first order kinetis is given by

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

Under the same assumption he obtained an equation for the second order kinetics and it is given by,

$$E = \frac{2KT^2_m}{T_2 - T_m} \qquad .. \qquad (4.24)$$

In the above equations, T_m is glow peak temperature and T_2 is temperature on high temperature side of glow peak at which intensity falls off to half of its peak value.

Chen(11) has suggested empirical correction factors of 0.976 and 0.853 for first order and second order kinetis respectively. Thus

$$E = 0.976 \frac{KT^2_m}{T_2 - T_m} \qquad .. \qquad (4.25) \text{ for first order kinetics}$$

and

$$E = 1.706 \frac{KT^2_m}{T_2 - T_m} \qquad .. \qquad (4.26) \text{ for second order kinetis}$$

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(12,13) considered the luminescene emission as mainly due to two kinds of recombination processes. In one process (sub model I of fig. 4.1) the electron is raised to an excited state with the forbidden gap below the conduction band, recombines with hole by tunneling process and in other, recombination takesplace via a conduction band (sub model II of fig. 4.1). If it is assumed that, the ratio ς ; 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 $\varsigma = 1$		
a) recombination dominant	$E_1 = \frac{KT^2_m}{T_2 - T_m}$	$\mu g \simeq e^{-1}$ .. (4.27)
b) Retrapping dominant	$E_2 = \frac{2KT^2_m}{T_2 - T_m}$	$\mu g \simeq 0.5$ .. (4.28)
Via conduction band $\cdot \simeq 1$		
a) First order Kinetics dominant	$E_3 = \frac{1.72\ KT^2_m}{T_m - T_1}(1 - \frac{5.16}{\Delta})$	$\mu_g \leqslant e^{-1}(1 + \frac{2}{\Delta})$ ..(4.29)
b) Second order Kineticsdominant	$E_4 = \frac{2KT^2_m}{T_m - T_1}(1 - \frac{6}{\Delta})$	$\mu g \ggg e^{-1}(1 + \frac{2}{\Delta})$ ..(4.30)

where $\frac{1}{\Delta} = \frac{KT_m}{E} << 1$ is a correction factor, and T_1 is the temperature on low temperature side of glow peak at which intensity is one half of its peak value.

$$\text{The factor } \mu g = \frac{\delta}{w} = \frac{T_2 - T_m}{T_2 - T_1}$$

is called the symmetry factor, and is a characteristic of the type of kinetics involved in the process.

$\mu g \leqslant e^{-1}(1 + \frac{2}{\Delta})$ for the first order kinetics

$\mu g \ggg e^{-1}(1 + \frac{2}{\Delta})$ for the 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 prescence of weak shoulders at the high temperature side of glow peak causes as apparent increase in the μg values which may wrongly indicate the process to be of the second order(14)The disadvantage is that E has to be evaluated in an iterative manner. One has to estimate E first by asuuming correction factor to be zero, then calculate the correction factor $\frac{1}{\Delta} = \frac{KT_m}{E}$ and then re-evaluate 'E'.

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

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

with condition $\mu g = 0.5$

Chen(11) has modified these formulae to avoid interaction and has given following equation. For first order kinetics,

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

and for seconds order kinetics

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

c) Method using full half width of the glow peak

(after Chen) :

Chen(11) has developed mathematical equations for E which make use of the full half width of a glow peak which can be measured with better experimental accuracy and he has given following relations

For first order Kinetics,

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

and for second order Kinetics

$$E = 2KT_m\left(\frac{1.756\ T_m}{T_2-T_m} - 1\right) \quad .. \quad (4.35)$$

Here numerial constants are chosen emperically to have a better estimation of E and $\frac{E}{KT_m} \gg 1$. Moreover Chen(15) showed that the symmetry factor $\mu g = 0.42$ is characteristic of first order peak and $\mu g = 0.52$ that of second order. On correlating the symmetry factor μg and order of kinetics α, he has given the following equations to evaluate E for general order Kinetics.

$$E = [\,1.51 + 3.0(\mu g - 0.42)\,]\,\frac{KT^2_m}{T_m - T_1} - [\,1.5 + 4.2(\mu g - 0.42)]\,2KT_m \qquad .. \quad (4.36)$$

$$E = [0.976 + 7.3(\mu g - 0.42)]\,\frac{KT^2_m}{T_2 - T_m} \qquad .. \quad (4.37)$$

$$E = [2.52 + 10.2(\mu g - 0.42)]\,\frac{KT^2_m}{T_2 - T_m} - 2KT_m \qquad .. \quad (4.38)$$

4.3.2 METHODS MAKING USE OF VARIOUS HEATING RATES

a) Method due to Booth, Bohum and Parfianovitch

Booth(16), Bohun (17) and Parfianovitch (18) have shown independently that, the activation energy can be determined without prior knowledge of frequency factor S. It can be determined by heating the phosphor at two different heating rates β_1, β_2. If $\beta_1 > \beta_2$ then $T_{m1} > T_{m2}$ where T_{m1} and T_{m2} are the corresponding values of glow peak temperature at two different heating rates β_1 and β_2.

Eliminating S from equation $\frac{E}{KT^2_m} = \frac{S}{\beta}\, e^{(-E/T_m k)}$

They found

$$E = \frac{KT_{m1}T_{m1}}{T_{m1} - T_{m2}} \quad \ln \frac{\beta_1 T^2_{m2}}{\beta_2\, T^2_{m1}} \qquad .. \quad (4.39)$$

If T_m can be measured within an accuracy of 1°K, the method is found to yield E within an error of 5% (19)

b) Method due to Schon

To achieve an improved accuracy in E values, Schon(20) modified the equation (4.39) by replacing T^2_m by $T_m^{3.5}$ which results in

$$E = \frac{K\, T_{m1}\, T_{m2}}{T_{m1} - T_{m2}} \; \ln \frac{\beta_1 T_{m2}^{3.5}}{\beta_2 T_{m1}^{3.5}} \qquad .. \qquad (4.40)$$

c) Method due to Chen and Winer

consider I_m to be the glow peak intensity corresponding to TL maximum obtained with heating rate β, Chen and Winer(21) have shown a plot of Ln $(I_{mi} T^4_{m1} / \beta_i^{\,2})$ versus $(1/T_{mi})$ yields a straight line with a slope equal to E/K. Knowing the slope; E can be evaluated.

d) Method due to Hoogenstraaten

Hoogenstraaten(22) has shown that the glow peak temperature Tm is related to E by the equation

$$Ln \frac{T_{m1}^{\;2}}{\beta i} = \frac{E}{KT_{mi}} + Ln \frac{E}{SK} \qquad .. \qquad (4.41)$$

Thus the plot between Ln $(T^2_{mi}2 \,/\, Bi)$ and $(1 \,/T_{mi})$ is linear with slope equal to E/K; from which E can be evaluated.

4.3.3 OTHER METHODS

a) Method due to Urbach

Urbach(23) derived independently from equation (4.7) an expression for activation energy by taking $S = 10^{\circ} sec^{-1}$

The equation is

$$E = T_m \,/\, 500 \qquad .. \qquad (4.42)$$

b) Method due to Randall and Wilkins

Randall and Wilkins(2) method is based on equatin (4.7) which assumes monomolecular kinetics and no retrapping. In this method, Tm corresponds to a temperature little below that at which frequency of an electron escaping the trap is one per second.This is given by

$$S \exp.(-E/KT_m)\ (1 + F(S,\beta) = 1 \qquad .. \qquad (4.43)$$

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

$$E = T_m\ (1 + F\ (S,\ \beta)\ K \log\ s \qquad .. \qquad (4.44)$$

where $F(S,\beta)$ is another function of S and β where, β lies between 0.5 and 2.5° K sec^{-1} and S equals the value

$2.9 \times 10^9\ sec^{-1}$, the above equation reduces to

$$E = 25\ K\ T_m \qquad .. \qquad (4.45)$$

c) Method due to Grosswiner

Grosswiner$^{(24)}$derived an equation for determining E, for first order kinetics as

$$E = \frac{1.51\ K\ T_m T_1}{T_m - T_1} \qquad .. \qquad (4.46)$$

According to him, this equation gives acurate results within ± 5% provided $S/\beta > 10^7\ {}^\circ k^{-1}$ and $E/KT_m > 20$.

Chen modified the Grosswiner's relation empirically giving

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

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

d) Method due to Dussel and Bube

Dussel and Bube$^{(25)}$ have shown that Grossweiner's method yields values of E which are above 7% higher for an improved accurancy, they suggested empirically.

$$E = C_8 \frac{KT_m T_1}{(T_m - T_1)} \qquad .. \qquad (4.48)$$

According to them when $E/KT_m = 17$, 22 or 26

C_8 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(4) is based on the fact that for all types of kinetics the intensity in the initial part of the glow curve can be expressed in the form.

$$I = Fe^{(-E/KT)} \qquad ... \qquad (4.49)$$

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

$$\log I = -E/KT + \text{constant} \qquad .. \qquad (4.50)$$

Hence the plot of Ln I versus $\frac{1}{T}$ (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 peak which yield 'E'without any knowledge of 'S' and is independent of recombination mechanism.

f) Method due to Nambi, Bapat and Ganguly

Activation energy can be determined by emperical formula developed by Nambi et al.(26) for $CaSO_4$: RE phosphors.

The relation between glow peak temperature 'Tm' and activation energy 'E' is given by

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

g) Numerical Kinetics Method

This method of analysis(27) 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 analyse 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 a specific temperature and at this temperature the luminescence decay is measured. This method has the advantage that such difficulties arising from overlapping of peaks and change in quantum efficiency or the emission spectra occuring under the nonisothermal conditions are avoided. The decay curve obtained can be analysed into sum of sharply defined linear region and it has been shown(28) that for the first order kinetics

$$I\ (T) = n_0 S \exp\ (-E/KT).\ \exp\ [S.te^{-E/KT}] \qquad .. \qquad (4.52)$$

where t is time.

Taking logarithms of equation (4.52) we have

$$\log I(T) = -se \exp\ (-E/KT) - E/KT + \log n_0 S \qquad .. \qquad (4.53)$$

Thus slope 'm' of log I (T) versus t curve is given by

$$M = s.e^{(-E/KT)} \qquad .. \qquad (4.54)$$

Taking the slopes m_1 and m_2 at two different temperatures T_1 & T_2 one can write

$$\mathrm{Ln}\ \frac{m_1}{m_2} = \frac{E}{K}\ \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \qquad .. \qquad (4.55)$$

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 ESCAPE FREQUENCY FACTOR (S)

The value of escape frequency factor 's' can be obtained from photo conductivity, Phosphorescence decay, dielectric relaxation measurement and thermoluminescence measurement. There exists several methods for determing S from TL and a brief survey is given below

4.4.1 METHOD DUE TO RANDALL AND WILKINS

Randall and Wilkin's$^{(2)}$ for the First order kinetics have given the general equation

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

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

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

$$\frac{E}{KT_m^2} = \frac{S}{\beta} e^{-E/KT_m} \quad .. \quad (4.57)$$

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

4.4.2 METHODS DUE TO GARLICK AND GIBSON

Following the second order kinetics the solution of equation $I = -dn/dt$, given by Garlick and Gibsen$^{(28)}$ with constant heating rate β is

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

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

$$1 + \frac{S'n_o}{\beta} \int_{T_o}^{T_m} e^{(-E/KT)} dT$$

$$= 2 \frac{KT^2_m}{\beta E} \; S \, n_o e^{(-E/KT_m)} \qquad .. \quad (4.59)$$

Assuming T_m to be the experimental peak temperature and with all other parameter in equation (4.59) are known, one can calculate the frequency factor $S = S_{no}$ for different values of E

4.4.3 ISOTHERMAL DECAY METHOD

The method suggested by Garlick(28) for the 1st order kinetics point that in an isothermal decay a plot of log I versus t may be regarded as a sum of sharply defined linear region. Slope m given by the equation. $m = se^{(-E/KT)}$. . By knowing E the frequency factor S can be calculated using equation

$$S = me^{(-E/KT)} \qquad .. \quad (4.60)$$

4.4.4 METHOD DUE TO ARAMU AND MAXIA

The method due to Aramu and Maxia(29) Starts from the kinetic equation and allows to determine the frequency factor by the use of simplified formula,

$$S = \beta \, e^{\eta} \qquad .. \quad (4.61)$$

Where β is heating rate and η isintercept with vertical axis of plot oflog 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(30) the glow peak temperature T_m and heating rate β are related to escape frequency factor, by the equation of the type.

$$\frac{S}{\beta} = \frac{2}{\delta} \left[e^{2T_m/\delta} \right] \qquad .. \quad (4.62)$$

where $\delta = T_2 - T_m$ is high temperature half width. Once the ratio of T_m/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$^{(37)}$ proposed the following equation on the assumption that density of free electrons (or holes in case of hole trap) is equal to the density of empty traps

$$\frac{1}{\tau} = \frac{2\pi m(KT)^2 \sqrt{6\pi}}{h^3} e^{-E/KT} \qquad .. \quad (4.63)$$

combining this equation with

$$P = \frac{1}{\tau} = Se^{-E/KT}$$

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

which in its simplest form is given as$^{(38)}$

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

Thus the values of σ can be estimated approximately.

4.6 RESULTS AND DISCUSSION

4.6.1 The TL glow curves are recorded by irradiating a Phosphor under uv as well as gamma irradiation. For uv irradiation (λ = 2.53 nm] a does of 15 minutes is given and heating rate used is 2.13°k/sec, while for gamma irradiation a dose of 25 minutes (2.1K Rad/min is given and the same heating rate is used. TL glow curves are recorded in temperature range from 313°K to 753°K. The temperature is changed with the help of linear temperature programmer fabricated in the laboratory. Details of instruments used are given in the Chapter II.

A) Glow Curves

TL glow curves are plotted for undoped $CaSO_4$, $CaSO_4$: Mn, $CaSO_4$:RE and $CaSO_4$: Mn : RE after uv as well as after gamma irradiation. It is observed that undoped $CaSO_4$ phosphor gives very weak peak for uv and gamma irradiation around 140°c, (fig.4.5)

When Mn is doped with $CaSO_4$, no significant peak is observed while with only $CaSO_4$ as host, a weak single peak is observed around 140°c under uv irradiation (Fig.4.5).Similarly under gamma irraidation small peak is observed for Mn doped phosphor.

When different rare earths (Dy, Nd, Eu, Tb) are doped with $CaSO_4$: Mn phosphor, under uv excitation are found to give peaks as shown in the figure (4.3), while under gamma irradiation they give the peaks as shown in the figure (4.4). The number of peaks in the glow curve indicates the different luminescent centres or different metastable states of the same centre(31).

It is observed that when rare earth is doped with $CaSO_4$:Mn phosphor,(36) peak intensity increases under gamma irradiation (fig.4.4) while under uv irradiation significant peak is observed for Dy,Eu,Nd,La (figure 4.3).

It is also seen that when Eu is doped with $CaSO_4$, first peak temperature is observed around 100°c and second peak temperature around 240°c (fig. 4.5). The same temperature is reported by previous workers(32,33)

It is also seen that, Eu doped $CaSO_4$:Mn phosphor gives a peak around 140°c under uv and gamma irradiation, while incase of other rare earths, doped with $CaSO_4$:Mn there is shift in peak temperature (from 140°C to 160°C) when excited under gamma irradiation (fig.4.4). It is further observed that, in presence of Eu, peak intensity of $CaSO_4$:Mn phosphor is increased (under uv excitation).

Thus from the study of TL glow curves for different rare earths Eu is the most suitable rare earth out of chosen (fig. 4.3., 4.4) Therefore, the effect of Eu and Mn concentration variation in $CaSO_4$ is further studied under uv and gamma irradiation.

i) Effect of uv irradiation on the phosphor

TL glow curves are studied under uv irradiation for different percentages of concentration of Eu and Mn doping in host $CaSO_4$. From these curves it is observed that, as the concentration of Eu goes on increasing (Mn 0.1% constant)glow peak intensity changes but the peak temperature remains unchanged (fig.4.6). Overall glow peak shape remains unchanged for very low concentration of Eu (0.001%), peak temperature is observed around 140°C and no second peak is observed (Table 4.1, fig. 4.6), while for 0.005% concentration of Eu peak intensity of first peak starts enhancing and second peak is observed around 240°C, while the first peak temperature remains unchanged (Table 4.1, fig. 4.6).

Upto a certain percentage of Eu concentration (0.05%) with constant Mn (0.1%) doping, first peak intensity goes on increasing, reaches to a maximum value and then starts decreasing but the peak temperature of this peak remains about 140°C and that of second peak remains about 240°C (Table 4.1, fig. 4.7, 4.8). The same peak temperatures are reported by previous workers (33). Beyond a certain concentration of Eu (0.2%) second peak is not observed (fig.4.8,Table 4.1).The optimum concentration of Eu is found to be 0.05%(Table 4.1 fig. 4.7).

When the concentration of Mn is changed, keeping percentage of Eu (0.1% constant), peak intensity changes while the peak temperature remains the same around 120°C to 140°C (fig.4.9, table 4.2).

When Mn percentage is increased upto 0.3% it is observed that, there is shift in first peak temperature to low temperatue side, from 140°c to 120°c, peak intensity is also reduced and a second peak is observed around 240°c (fig. 4.9, table 4.2). The second peak is observed upto 1% concentration of Mn (fig.4.9, 4.10)

It is also seen that, in the absence of second peak intensity of first peak is more. When the concentration of Mn equal to 0.05% The optimum concentration of Mn observed is 0.1% (Table 4.2).

The above observations indicate that, peak around 140°c is probably due to the host CaSO$_4$. The presence of Eu in the host is found to enhance the TL intensity of this peak and also second peak around 240°c.

Double doping with typical concentration gives rise to two peaks with increase of TL output till the concentration of Mn (1 %) and Eu (0.1%) is obtained, beyond which 140°c peak only persists and second peak is not observed. This behaviour in particular is quite different from that observed in earlier studies for same phosphor(33) .

In case of other rare earths in CaSO$_4$:Mn, peak intensity of 240°c is higher than that of 100°c, for gamma irradiated phosphor(33) The traps responsible in CaSO$_4$: Mn : Eu phosphor for 240°c peak are seen to be of different origin than those provided in case of other rare earth. Probably high temperature peak traps may not be getting excited under uv irradiation.

Mechanism of energy transfer if any in present work requires further critical study and use of other experimental tools. However, in present study such an attempt is not made.

In the present study two peaks, one around 140°c and other around 240°c are found to be present only for certain range of concentrations of Mn:Eu. Maximum TL output being for Mn 0.1% and Eu 0.05%.

In earlier studies (33) it is reported that Mn:Eu double doping gives a single peak. This is probably due to the fact that earlier workers have recorded TL glow curves for fixed concentration of Mn:Eu.

The present work therefore indicates that, for certain typical concentration second peak around 240°c is obtained even for low energy radiations like uv For such concentrations, traps responsible for high temp. (240°c) peak are more populated. For still higher concentrations of dopants the effect is like quenching.

Careful observatins of TL glow curves of various concentrations of Mn and Eu indicate the possibility of energy transfer to an extent. These findings are in line with exhaustive work reported on energy transfer of the same phosphor by V.N.Bapat (33). However detailed study of energy transfer is not further carried out in present work.

2) <u>Effect of gamma irradiation on the phosphors</u>

TL glow curves are studied also after gamma irradiation of the same phosphors (fig. 4.11 to 4.13).

Eu:Mn doped phosphors under gamma irradiation are found to to give again a single peak around 140°c indicating similar traps as in uv studies. Dy:,Mn, Tb:Mn, Gd:Mn doped phosphors under gamma irradiation are found to give two peaks, first around 160°c and higher temperature peak around 340°c (fig.4.4) other rare earths give a single peak as for uv irradiated samples.

Glow curve is studied after gamma irradiation for various concentraions of Eu, while keeping the concentration of Mn constant(0.1%). It is observed that, as the concentratin of Eu goes on increasing from 0.001% to 0.01% intensity of peak goes on increasing and reaches to a maximum value and then decreases (fig. 4.11 to 4.13, Table 4.3). Optimum concentration of Eu under gamma irradiation is found to be 0.01% . It is also observed that for $CaSO_4$:Mn:Eu doped phosphor on gamma irradiation,there is no shift in the peak temperature. A single peak is observed around 140°c. This peak can be attributed to the host and that TL output is incrased by addition of Mn & Eu

The presence of single peak in case of Mn:Eu phosphor, indicates no possibility of energy transfer from high temperature to low temperature peak as found in Dy:Mn, Tb:Mn, Gd:Mn (33) .In case of other rare earths in presence of Mn also the first peak temperature is found to be shifted to the higher temperature side (140°c to 160°c.)

As seen from the figure (fig.4.4) after gamma irradiation, activators like Dy, Tb, Gd in presence of Mn are found to be promising. These findings are in agreement with those by earlier workers(32,33)

From the present study it is indicative that Eu, Sm, Nd may prove as promising activators in presence of Mn in uv irradiation.

Study of TL glow curves after uv irradiation reveals that $CaSO_4$: Mn:Eu is the most suitable phosphor but Dy, Tb doped phosphors may not prove to be so.

Invariably $CaSO_4$:Mn:Eu phosphor gives a single peak practically arund 140°c for gamma irradiation.

From the study of concentration variation (Table 4.3, fig. 4.14) after gamma irradiation optimum concentration of Eu is found to be 0.01% while in uv irradiated samples optimum concentration of Eu is found to be 0.05% (Table 4.1, fig. 4.15).

B) Activatin Energy

The activation energies are calculated using different methods as described in sectin 4.3.

In the present study, activation energies are calculated from the shape of the TL glow curve by using methods given by (i) Urbach(1) (ii) Lushick(10) (iii) Halperin and Braner(12,13) (iv) Chen (11) (v) Gross Weiner (24). The activation energies are calculated for uv irradiated and gamma irradiated samples of different percentage of concentrations of Mn and Eu.These values are listed in the table 4.5 to 4.7. There is no significant variation in the activation energy of uv, gamma excited samples.The activation energy lies in the range of 0.6eV to 1eV

Activation energies are also calculated for uv irradiated sample ($CaSO_4Mn_{0.1}$ $Eu_{0.1}$) using different rate of heating (equation 4.34). These values listed in the table (4.8) lie in the range of 0.7eV to 1.7eV which is constant.

An attempt is also made to find the activation energy by initial rise method for a typical sample of composition $CaSO_4$:$Mn_{0.1}$:$Eu_{0.1}$ Arrhenius plots(34) are shown in the fig. (4.16).The activation energy calculated by this method is 0.6624 eV.

c) Variation of activation energy with activator concentration

It is seen from table (4.5 to 4.7) that activation energy does not vary significantly with activator concentration both for uv and gamma irradiation. The effective trap levels are distributed from 0.75eV to 1.2eV for uv irradiation and that from 0.9eV to 1.2eV for gamma irradiation. The observed variation is not systematic with respect to concentration variation. This suggests that addition of rare-earths as an activator does not introduce any new traps but modifies the relative importance of traps responsible for TL (39, 40)

d) Kinetics of luminescence

The value of symmetry factor μg determines the kinetics involved in the process. These values are listed in table (4.5 to 4.7). From the table it is observed that $\mu g > \frac{1}{e}$. This indicates that order of kinetics may be of II order for uv and gamma irradiated phosphor.

e) Escape frequency factor (S)

The escape frequency factor (S) is calculated by using equation (4.8). The values of 's' obtained are mainly dependent upon 'E'. 'S' values are calculated with activation energies using Luschik formula and Urbach formula. The values are listed in the table 4.5 to 4.7. Values of 'S' vary from 10^5 sec^{-1} to 10^{13} sec^{-1} for uv irradiated samples and those vary from 10^8 sec^{-1} to 10^{13} sec^{-1} for gamma irradiated samples. However, no special significance can be attended to these findings.

f) Size of Traps

The capture cross section (σ) of each type of trapping centre can be evaluated from the knowledge of escape frequency factor. The values of σ are calculated by using equation 4.64. The values are listed in table 4.5 to 4.7. The size of trap is in the range of 10^{-13}cm^2 to 10^{-21}cm^2 for uv excited samples and that of 10^{-13}cm^2 to 10^{-18} cm^2

for gamma excited samples. The traps in present investigation may be regarded as medium size traps (35)

C) Dose Dependence

Peak intensity of a glow curve is found to be a function of excitation dose. The glow curve for various excitation time is shown in the figure (4.17, 4.19) and the plots of glow peak intensity versus duration of excitation are shown in figure 4.18 and fig. 4.20 for a sample under uv and gamma irradiation. It is observed that for uv excited phosphor, peak intensity of a glow curve initially increases sublinearly and approaches to saturation rapidly while for gamma excited phosphor peak intensity of a glow curve increases and reaches to a maximum value (15 minutes irradiation) and then decreases.

4.7 SUMMARY

The important features of this chapter can be summarised as follows :

1] The overall shape of the glow curve is not significantly affected by variation of activator concentration, as well as by changing activator itself for uv and also for gamma irradiated samples. While the peak intensities are significantly influenced by activators (Mn, Eu).

2] Addition of activators does not give new glow peaks in the temperature region studied, under uv and gamma irradiation.

3] Optimum concentration of Eu is observed 0.05% under uv excitation while that for gamma excitation is 0.01%, optimum concentration of Mn is observed 0.1% under uv excitation.

4] Two peaks are observed for typical concentrations of Mn:Eu

5] The probable kinetics involved in TL process may be of the second order.

6] Trap depths of effective levels are insensitive to the concentration activators (Mn,Eu). They are in the range of 10^{-13}cm^2 to 10^{-18} cm^2 for gamma irradiation while 10^{-13}cm^2 to 10^{-21}cm^2 for uv irradiation. Traps in present investigation may be tegarded as medium size traps.

7] The glow peak intensity is a function of excitation time.

8] The activators do not seem to generate new traps but are responsible in increasing relative importance of existing traps as such these phosphors can be used in uv dosimetry.

TABLE No.4.1.

Peak temperature and Peak intensity values obtained from TL glow curves of $CaSO_4$:Mn:Eu phosphor (Mn 0.1%) under uv. excitation

Sample No.	%Eu	First peak temp. °c.	First Peak intensity (Arb.Units)	Second Peak temperature °c	Second Peak intensity (Arb.units)
PD 13	0.001%	140	13	--	--
PD 14	0.005%	140	32	240	8
PD 15	0.01%	140	128	240	85
PD 16	0.05%	140	218	240	110
PD 26	0.1%	140	178	240	135
PD 17	0.2%	140	88	--	--
PD 18	0.5%	140	35	--	--
PD 19	1%	140	19	--	--
PD 20	5%	140	7	--	--

TABLE 4.2

Peak temperature and peak intensity values obtained from TL glow curves of $CaSO_4$:Mn:Eu phosphor (Eu 0.1%) under uv excitation

Sample No.	Mn %	First peak temp. °c.	First peak intensity (Arb.units)	Second peak temperature °c	Second peak intensity (Arb.units)
PD 21	0.05%	120	200	--	---
PD 12	0.1%	140	280	240	118
PD 22	0.3%	120	108	220	42
PD 23	0.5%	120	108	240	88
PD 24	1%	120	108	220	42
PD 25	5%	120	11	--	--

TABLE 4.3

Peak temperature and Peak intensity values obtained from TL glow curves of $CaSO_4$:Mn:Eu phosphor (Mn 0.1%) under gamma excitation

Sample No.	% Eu	Peak temp. °c.	Peak intensity x 10^3 (Arb.Units)
PD 13	0.001%	140	74
PD 14	0.005%	140	82
PD 15	0.01%	140	85
PD 16	0.05%	140	40
PD 26	0.1%	140	16
PD 17	0.2%	140	17.9
PD 18	0.5%	140	9
PD 19	1%	140	8
PD 20	5%	140	0.5

TABLE NO.4.4

Peak temperature and Peak intensity values obtained from TL glow curves of $CaSO_4$:Mn:RE phosphor (Mn 0.1%) under gamma excitation

Sample No	R.E. %	First peak temp. °c	First peak intensity x10^3 (Arb.units)	Second peak temperature °c	Second Peak intensity x 10^3 (Arb.units)
PD 1	Undoped $CaSO_4$	140	8.5	--	--
PD 3	Tb 0.1% (Mn Absent)	160	89	320	48.5
PD 5	Dy 0.1%	160	97	340	85
PD 6	Tb 0.1%	160	28.3	340	8
PD 7	Y 0.1%	160	47.2	--	--
PD 8	Gd 0.1%	160	54.8	340	16
PD 9	Sm 0.1%	160	85.5	--	--
PD 10	Nd 0.1%	160	84.3	--	--
PD 4	Eu 0.1% (Mn absent)	100	130	240	--

TABLE 4.5

T.L. Parameters :- Activation Energies, Frequency factor, and size of trap of UV excited phosphor CaSO4:Mn:Eu (Mn 0.1%)

								ACTIVATION ENERGIES					FREQUENCY FACTOR		SIZE OF TRAP	
Sample No.	% Eu	Im Arb. units	TM ^{0}k	T1 ^{0}k	T2 ^{0}k	µg	order of kinetics	Eu ev	ELc ev	EHBC ev	EGC ev	Ec ev	Su sec^{-1}	SHBC SEC^{-1}	σu cm^2	σHBC cm^2
PD13	0.001%	13	413	377	485	0.67	II	0.83	0.35	0.60	0.63	0.40	1.58X10^{9}	1.79X10^{6}	1.05X10^{-17}	1.19X10^{-20}
PD14	0.005%	32	413	389	441	0.54	II	0.83	0.90	0.97	0.97	0.91	1.58X10^{9}	9.41X10^{10}	1.05X10^{-17}	6.27X10^{-16}
PD15	0.01 %	128	413	381	461	0.60	II	0.83	0.52	0.69	0.71	0.56	1.58X10^{9}	2.57X10^{7}	1.05X10^{-17}	1.71X10^{-19}
PD16	0.05 %	218	413	381	473	0.65	II	0.83	0.42	0.69	0.71	0.48	1.58X10^{9}	2.57X10^{7}	1.05X10^{-17}	1.71X10^{-19}
PD26	0.1 %	178	413	389	489	0.76	II	0.83	0.33	0.97	0.97	0.44	1.58X10^{9}	9.41X10^{10}	1.05X10^{-17}	6.27X10^{-16}
PD17	0.2 %	88	413	389	461	0.66	II	0.83	0.52	0.97	0.97	0.64	1.58X10^{9}	9.41X10^{10}	1.05X10^{-17}	6.27X10^{-16}
PD18	0.5 %	35	413	373	457	0.52	II	0.83	0.57	0.53	0.56	0.53	1.58X10^{9}	2.22X10^{5}	1.05X10^{-17}	1.48X10^{-20}
PD19	1 %	19	413	373	493	0.66	II	0.83	0.31	0.53	0.56	0.35	1.58X10^{9}	2.22X10^{5}	1.05X10^{-17}	1.48X10^{-21}
PD20	5 %	7	413	353	453	0.4	II	0.83	0.63	0.30	0.35	0.44	1.58X10^{9}	1.97X10^{2}	1.05X10^{-17}	1.31X10^{-24}
PD4	0.1 % (Mn a-bsent)	128	373	349	397	0.50	II	0.75	0.85	0.78	0.79	0.81	1.77X10^{9}	4.69X10^{9}	1.17X10^{-17}	3.12X10^{-17}

Tm - Peak temperature ^{0}K.
Im - Peak currrent (Arb:units)
EU - Energy calculated from Urbach formula.
ELC - Energy calculated from Luschik. formula with Chen´s correction.
EHBC - Energy calculted from Halperin & Braner formula with chen´s correction.
Ec - Energy calculated from Chen´s formula.
EGC - Energy calculated from Grosswiener formula with Chen´s correction.
SU´ - Escape frequency factor calculated using activation energy Eu
SHBC - Escape frequecy factor calculated using activation energy E^{HBC}.
σU - Size of trap depth using S^{U}.
σHBC - Size of trap depth usiing S^{HBC}.

TABLE 4.6

T.L. Parameters :- Activation Energies, Frequency factor, and size of trap of gamma excited phosphor CaSO4:Mn:Eu(Mn 0.1%)

								ACTIVATION ENERGIES					FREQUENCY FACTOR		SIZE OF TRAP	
Sample No.	% Eu	$I_m \times 10^3$ Arb. units	T^M 0k	T^1 0k	T2 0k	μg	order of kinetics	Eu ev	ELc ev	EHBC ev	EGC ev	Ec ev	Su sec^{-1}	SHBC sec^{-1}	σu cm^2	σHBC cm^2
PD13	0.001%	74.1	413	393	465	0.72	II	0.83	0.48	1.19	1.179	0.64	$1.58X10^9$	$5.55X10^{13}$	$1.05X10^{-17}$	$3.69X10^{-13}$
PD14	0.005%	81.5	413	385	509	0.77	II	0.83	0.26	0.81	0.825	0.34	$1.58X10^9$	$5.1 X10^8$	$1.05X10^{-17}$	$3.4 X10^{-18}$
PD15	0.01 %	84.5	413	389	529	0.83	II	0.83	0.22	0.97	0.97	0.29	$1.58X10^9$	$9.41X10^{10}$	$1.05X10^{-17}$	$6.27X10^{-16}$
PD16	0.05 %	39.8	413	389	485	0.75	II	0.83	0.35	0.97	0.97	0.46	$1.58X10^9$	$9.41X10^{10}$	$1.05X10^{-17}$	$6.27X10^{-16}$
PD17	0.2 %	17.9	413	393	473	0.75	II	0.83	0.42	1.19	1.179	0.56	$1.58X10^9$	$5.5 X10^{13}$	$1.05X10^{-17}$	$3.69X10^{-13}$
PD18	0.5 %	9	413	393	473	0.75	II	0.83	0.42	1.19	1.179	0.56	$1.58X10^9$	$5.5 X10^{13}$	$1.05X10^{-17}$	$3.69X10^{-13}$
PD19	1 %	8	413	401	513	0.89	II	0.83	0.25	1.22	2	0.38	$1.58X10^9$	$9.22X10^{13}$	$1.05X10^{-17}$	$6.14X10^{-13}$
PD20	5 %	0.5	413													

TABLE 4.7

T.L. Parameters :- Activation Energies, Frequency factor, and size of trap of UV excited phosphor $CaSO_4$:Mn:Eu(Eu 0.1%)

								ACTIVATION ENERGIES					FREQUENCY FACTOR		SIZE OF TRAP	
Sample No.	% Eu	Im Arb. units	TM 0k	T1 0k	T2 0k	μg	order of kinetics	Eu ev	Elc ev	E_{HBC} ev	EGC ev	Ec ev	Su sec^{-1}	S_{HBC} sec^{-1}	σ_u cm^2	σ_{HBC} cm^2
PD21	0.05 %	198	413	373	445	0.44	II	0.83	0.78	0.53	0.56	0.64	$1.58X10^9$	$2.22X10^5$	$1.05X10^{-17}$	$1.48X10^{-21}$
PD12	0.1 %	280	413	393	485	0.78	II	0.83	0.35	1.19	1.18	0.48	$1.58X10^9$	$5.55X10^{13}$	$5.1X10^{-17}$	$3.69X10^{-13}$
PD22	0.3 %	108	393	373	445	0.72	II	0.79	0.44	1.07	1.06	0.58	$1.67X10^9$	$8.76X10^{12}$	$9.41X10^{-17}$	$5.83X10^{-14}$
PD23	0.5 %	108	413	393	517	0.83	II	0.83	0.24	1.19	1.18	0.34	$1.58X10^9$	$5.55X10^{13}$	$1.05X10^{-17}$	$3.69X10^{-13}$
PD24	1 %	108	393	373	437	0.69	II	0.79	0.52	1.07	1.06	0.68	$1.67X10^9$	$8.76X10^{12}$	$1.11X10^{-17}$	$5.83X10^{-14}$
PD25	5 %	11	393	373	445	0.72	II	0.79	0.44	1.07	1.06	0.60	$1.67X10^9$	$8.76X10^{12}$	$1.11X10^{-17}$	$5.83X10^{-14}$

TABLE 4.8

Activation energies calculated from different rate of heating method for $CaSO_4$:Mn 0.1:Eu 0.1 phosphor after uv excitation

Heating rate °c/sec	Peak temp. °C	Peak temp °K	E eV
1.35	140	413	1.46
10.6	160	433	
10.6	160	433	1.69
14.49	140	413	
3.57	140	413	1.17
19.23	160	433	
3.57	140	413	0.71
10.6	160	433	

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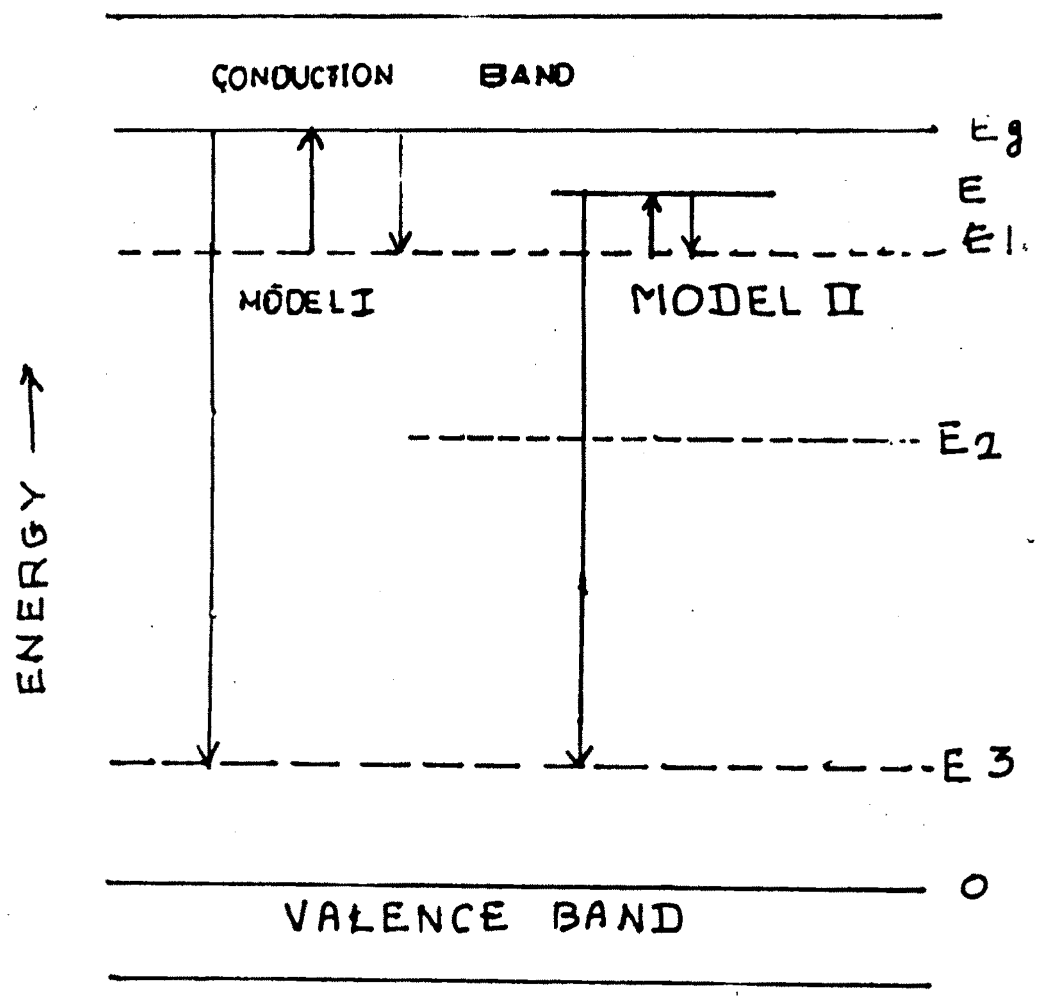


ENERGY BAND MODEL OF THERMOLUMINESCENCE FIG 4·1

UV EXCITED SAMPLE

GLOW CURVE FOR $CaSO_4$:Mn:Eu PHOSPHOR.

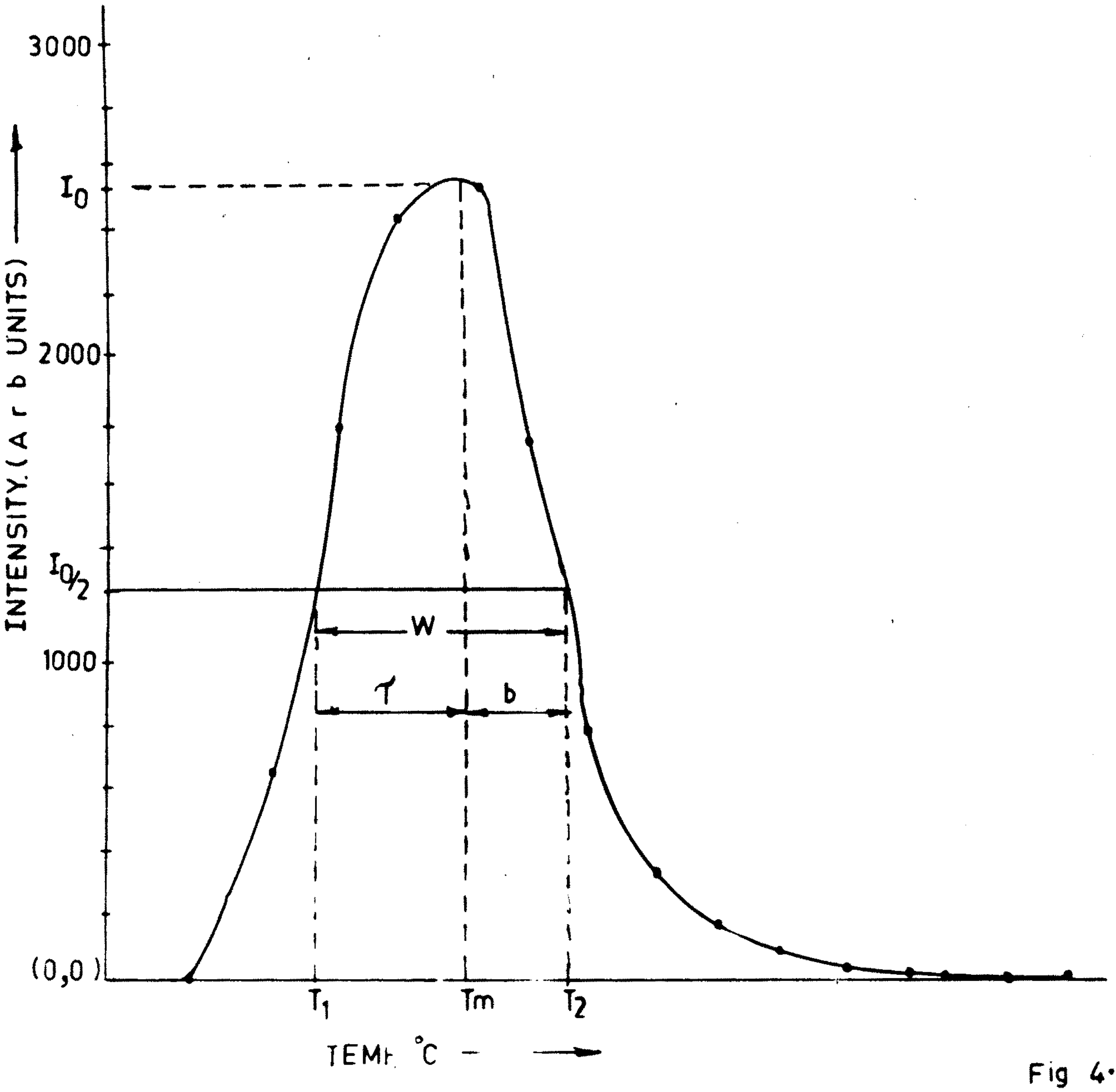


Fig 4·2.

TL GLOW CURVES WITH DIFFERENT RARE EARTHS AS SECOND ACTIVATOR FOR UV EXCITED SAMPLES.

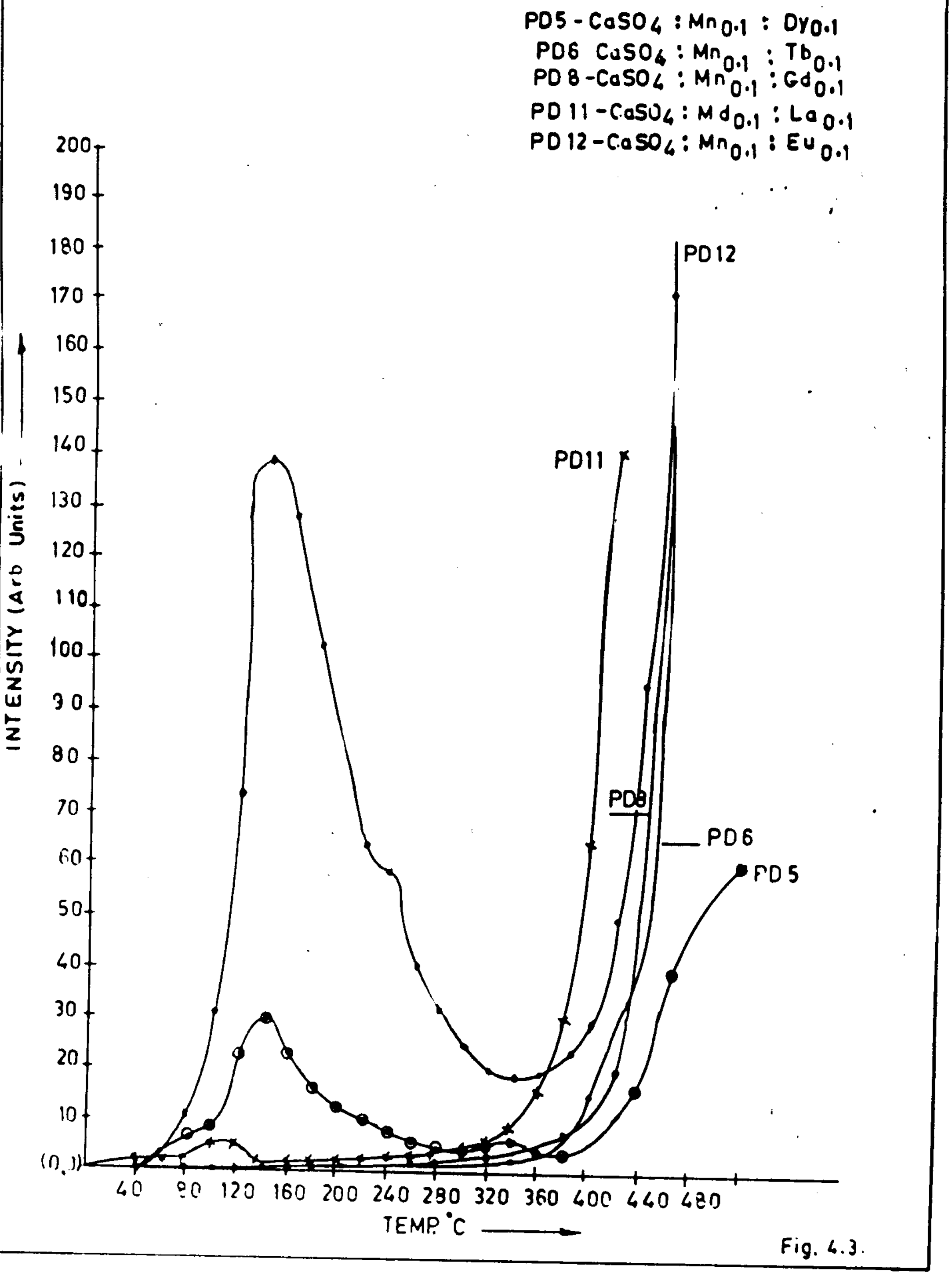


Fig. 4.3.

TL GLOW CURVES WITH DIFFERENT RARE EARTHS AS SECOND ACTIVATOR FOR GAMMA EXCITED SAMPLES

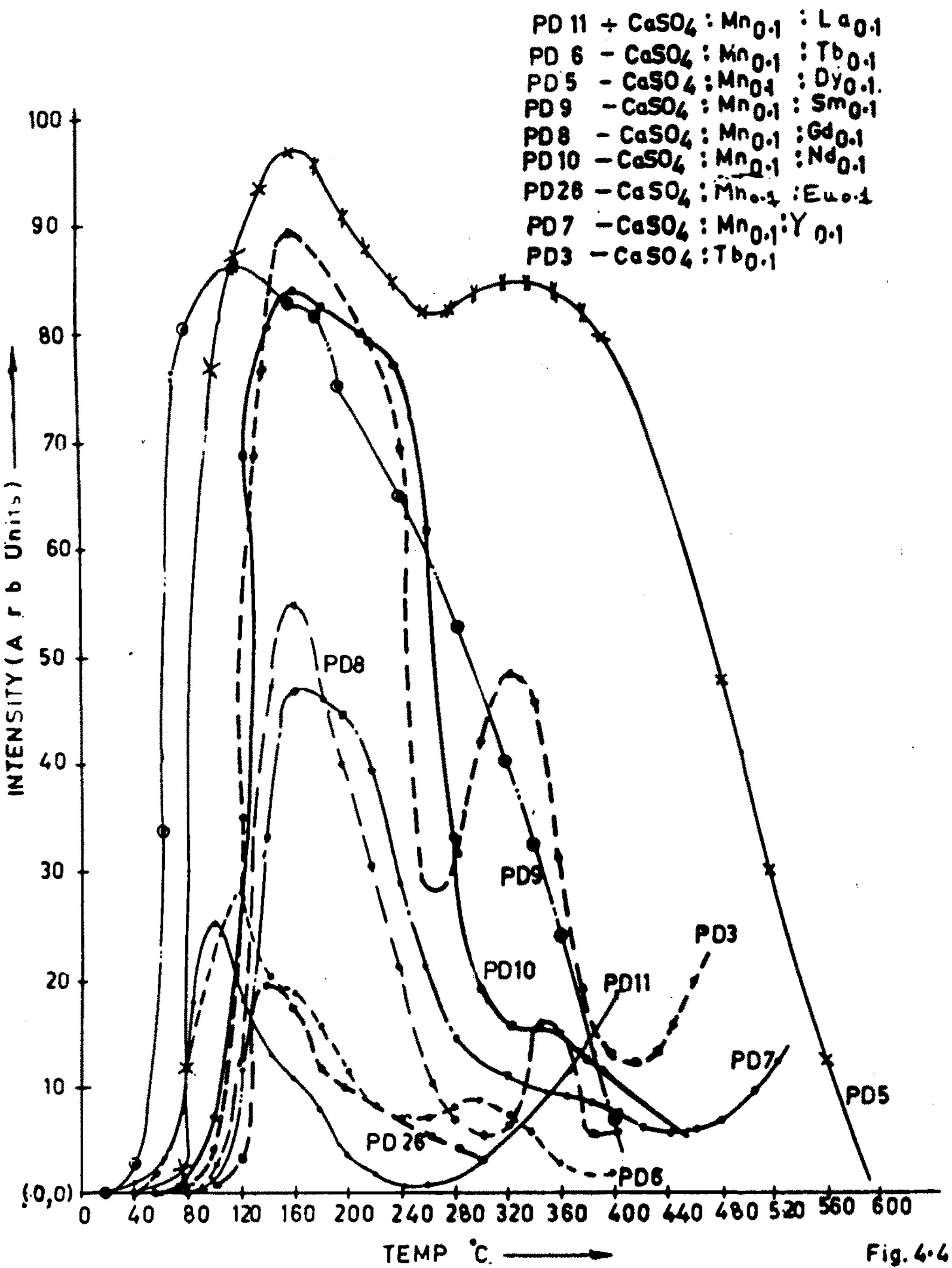


Fig. 4·4

TL GLOW CURVES OF UNDOPED AND DOPED PHOSPHORS UNDER UV EXCITATION.

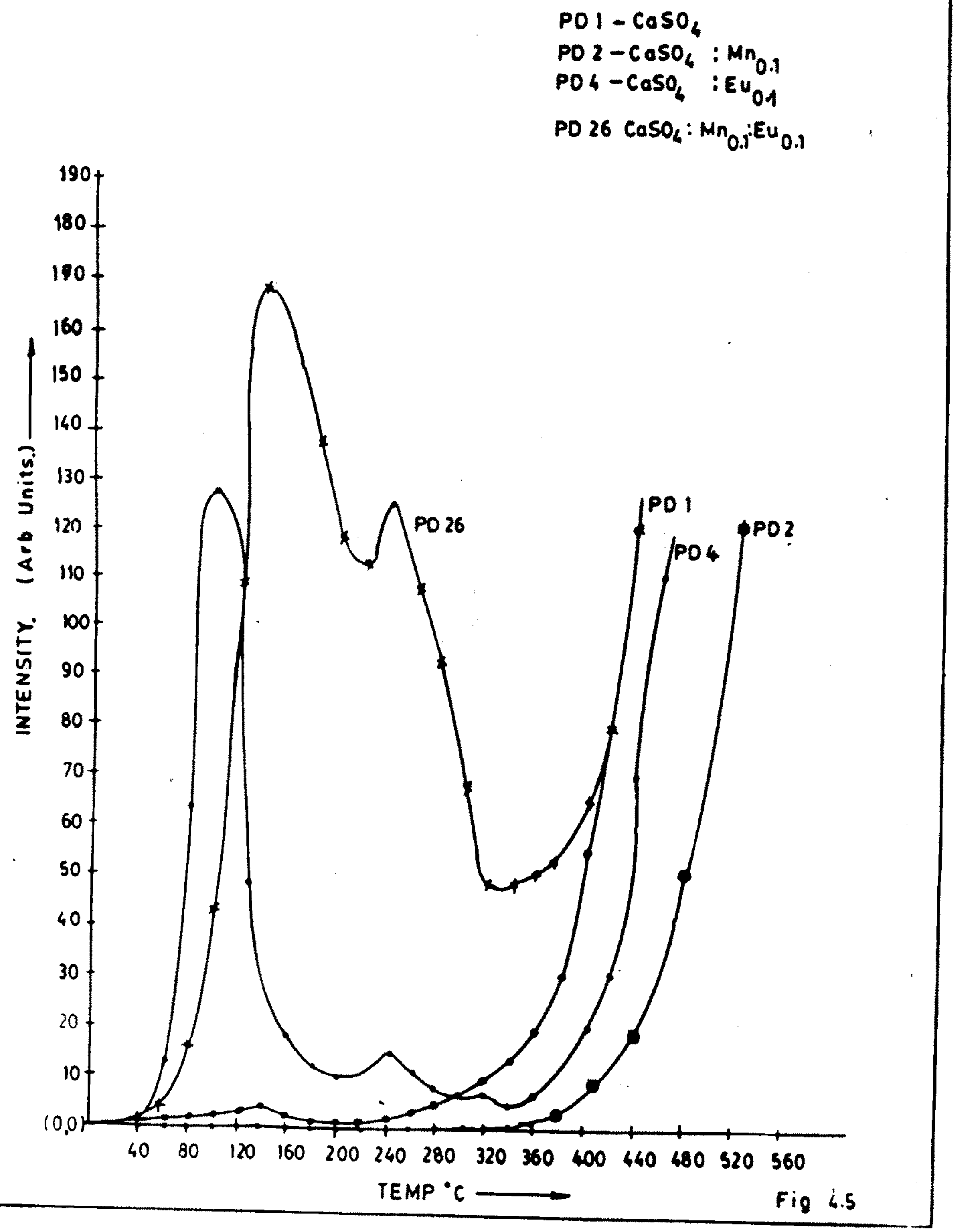


Fig 4.5

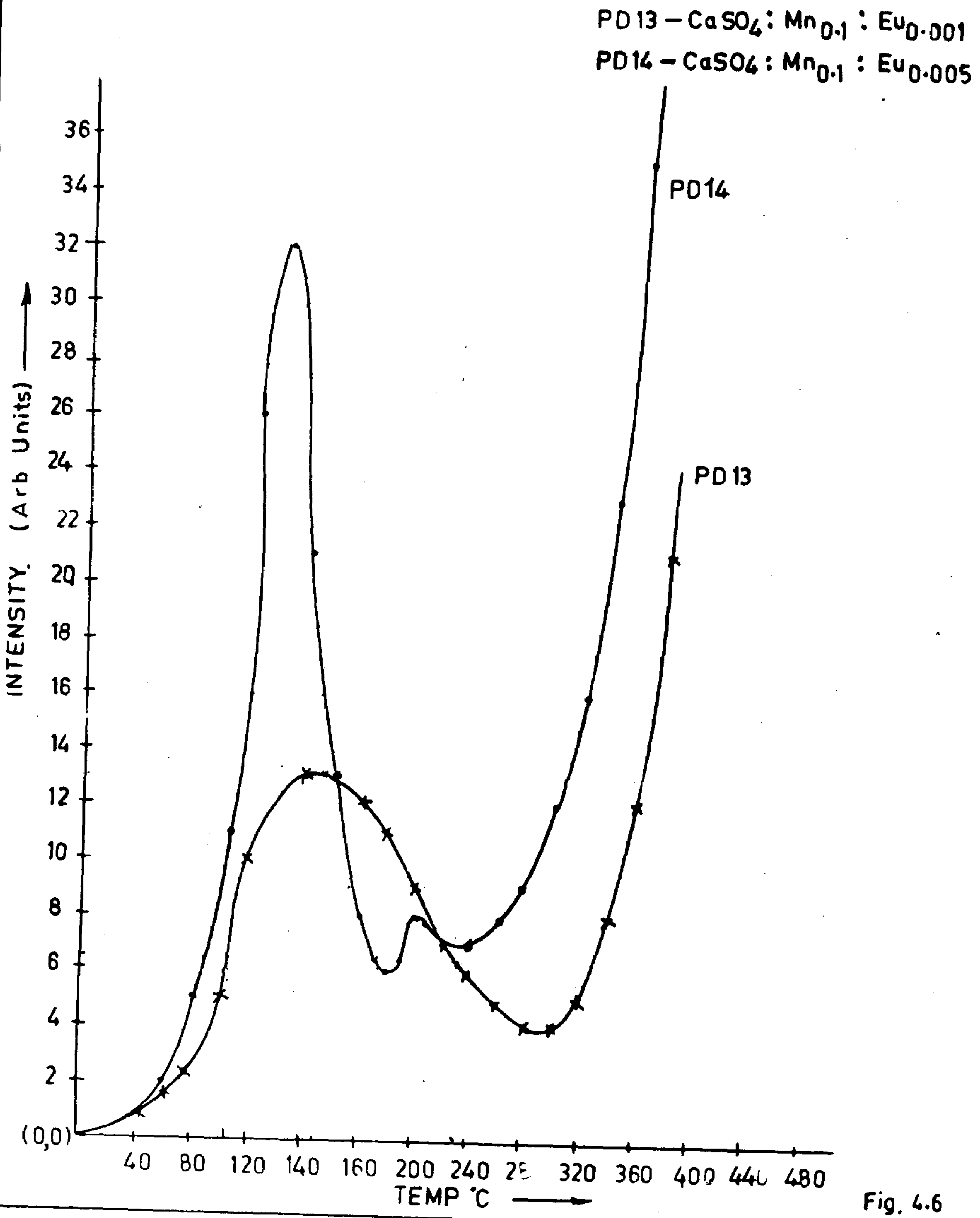

TL GLOW CURVES OF $CaSO_4$ Mn Eu PHOSPHOR OF DIFFERENT CONCENTRATION UNDER UV EXCITATION

Fig. 4.6

TL GLOW CURVES OF $CaSO_4$: Mn : Eu PHOSPHOR OF DIFFERENT CONCENTRATION UNDER UV EXCITATION.

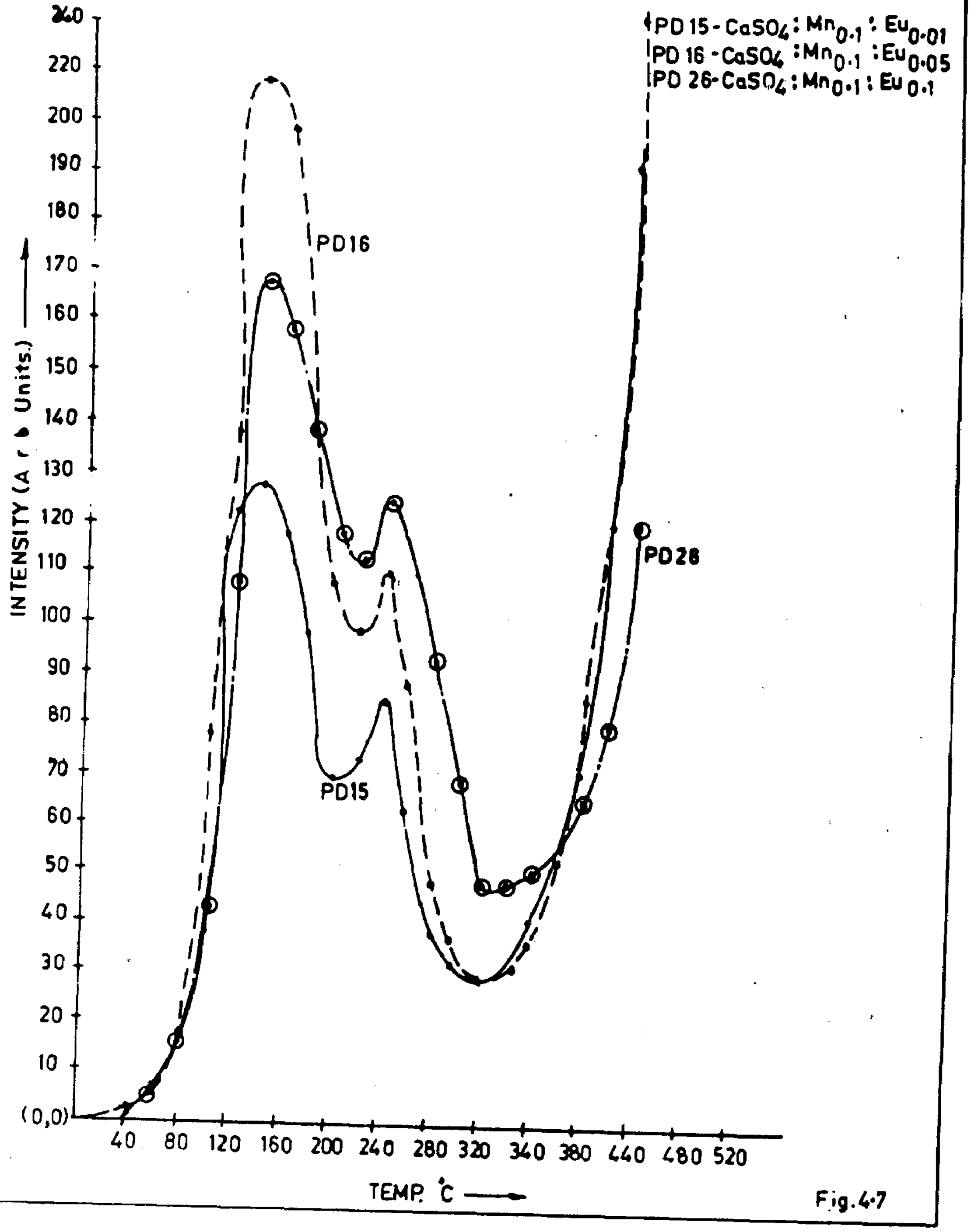


Fig.4·7

TL GLOW CURVES OF $CaSO_4$: Mn : Eu PHOSPHOR OF DIFFERENT CONCENTRATION UNDER UV EXCITATION.

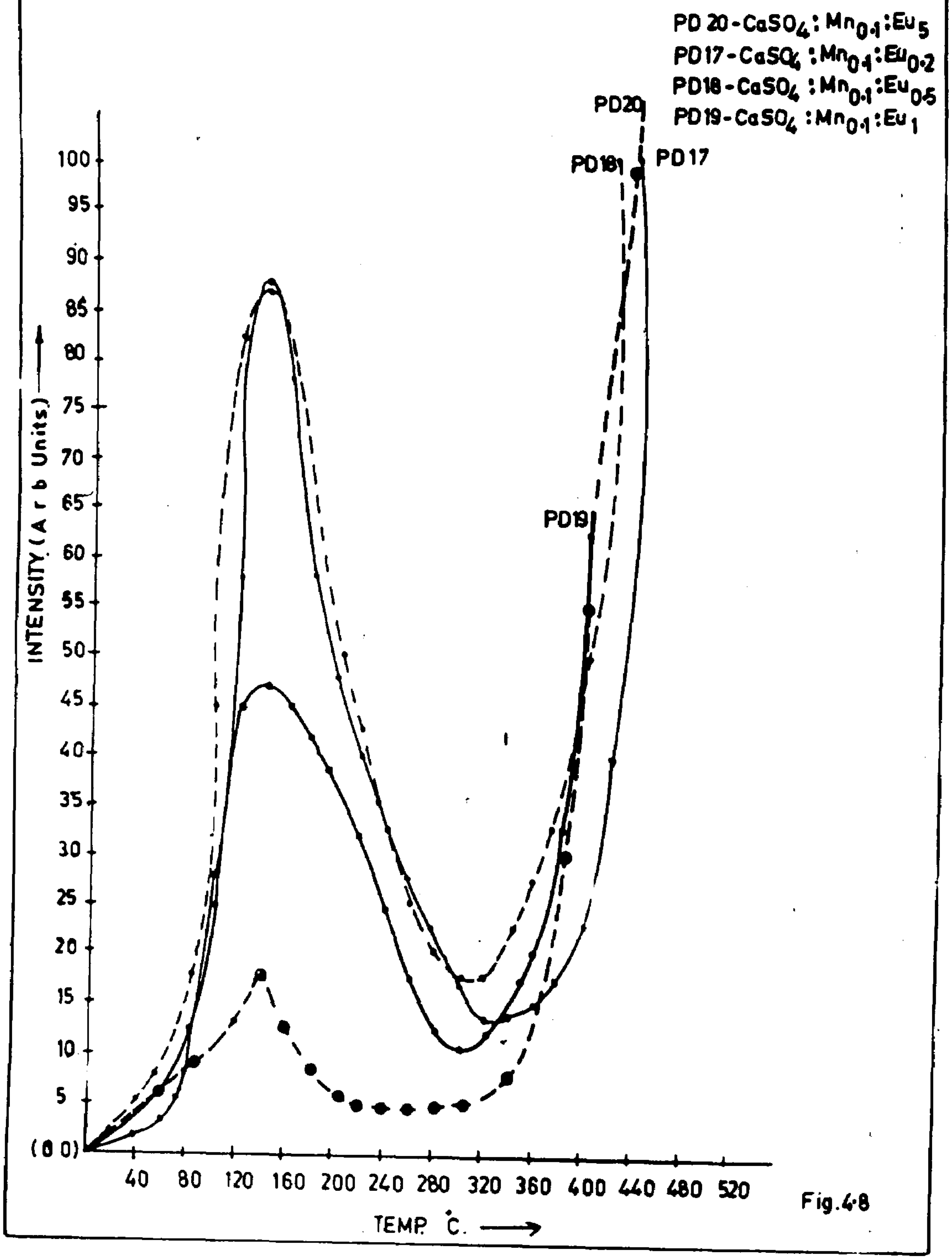
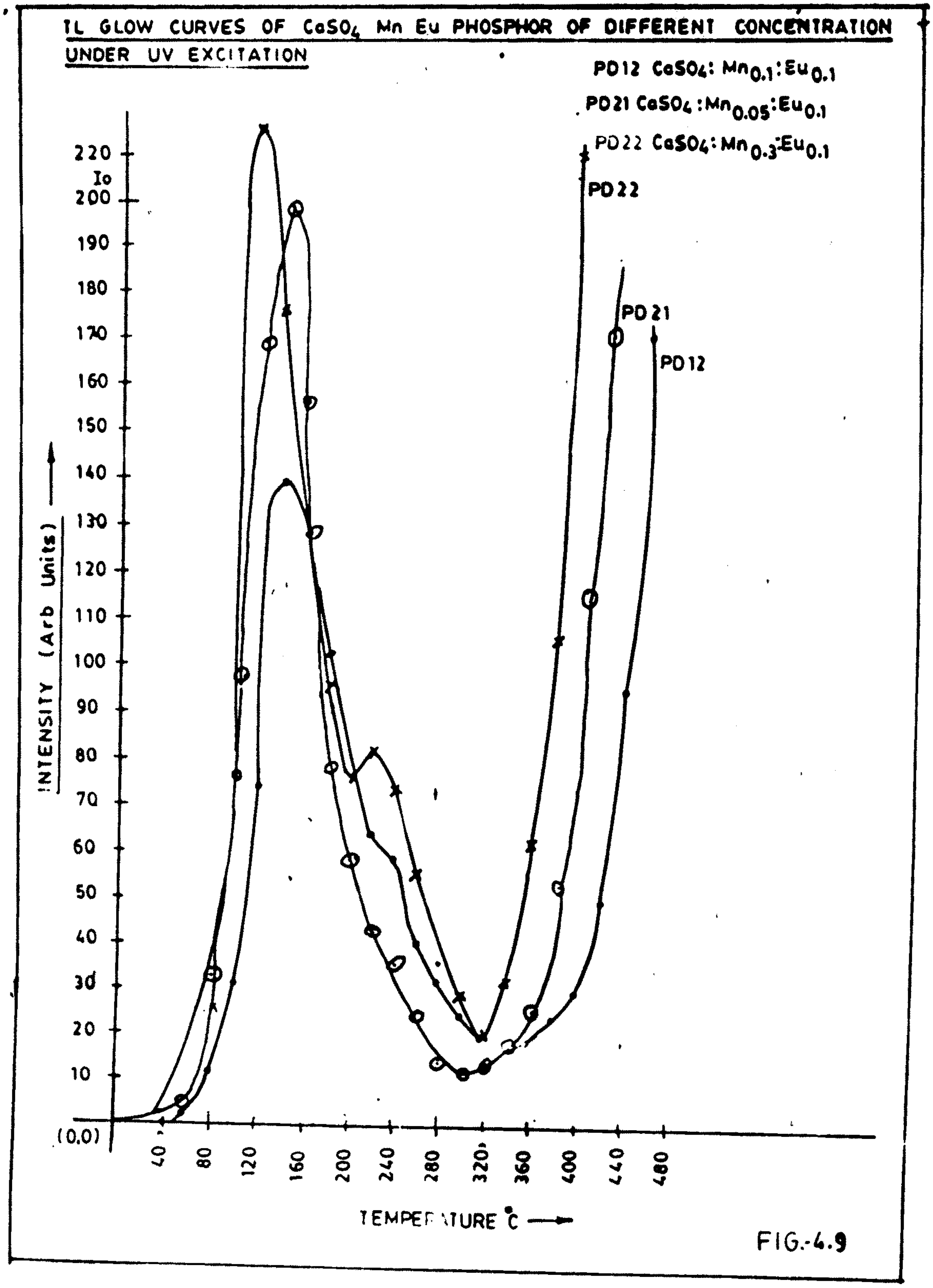


Fig.4·8



TL GLOW CURVES OF $CaSO_4$ Mn Eu PHOSPHOR OF DIFFERENT CONCENTRATION UNDER UV EXCITATION

FIG.-4.9

TL GLOW CURVES OF $CaSO_4$: Mn : Eu ' PHOSPHOR OF DIFFERENT CONCENTRATION UNDER UV EXCIATION

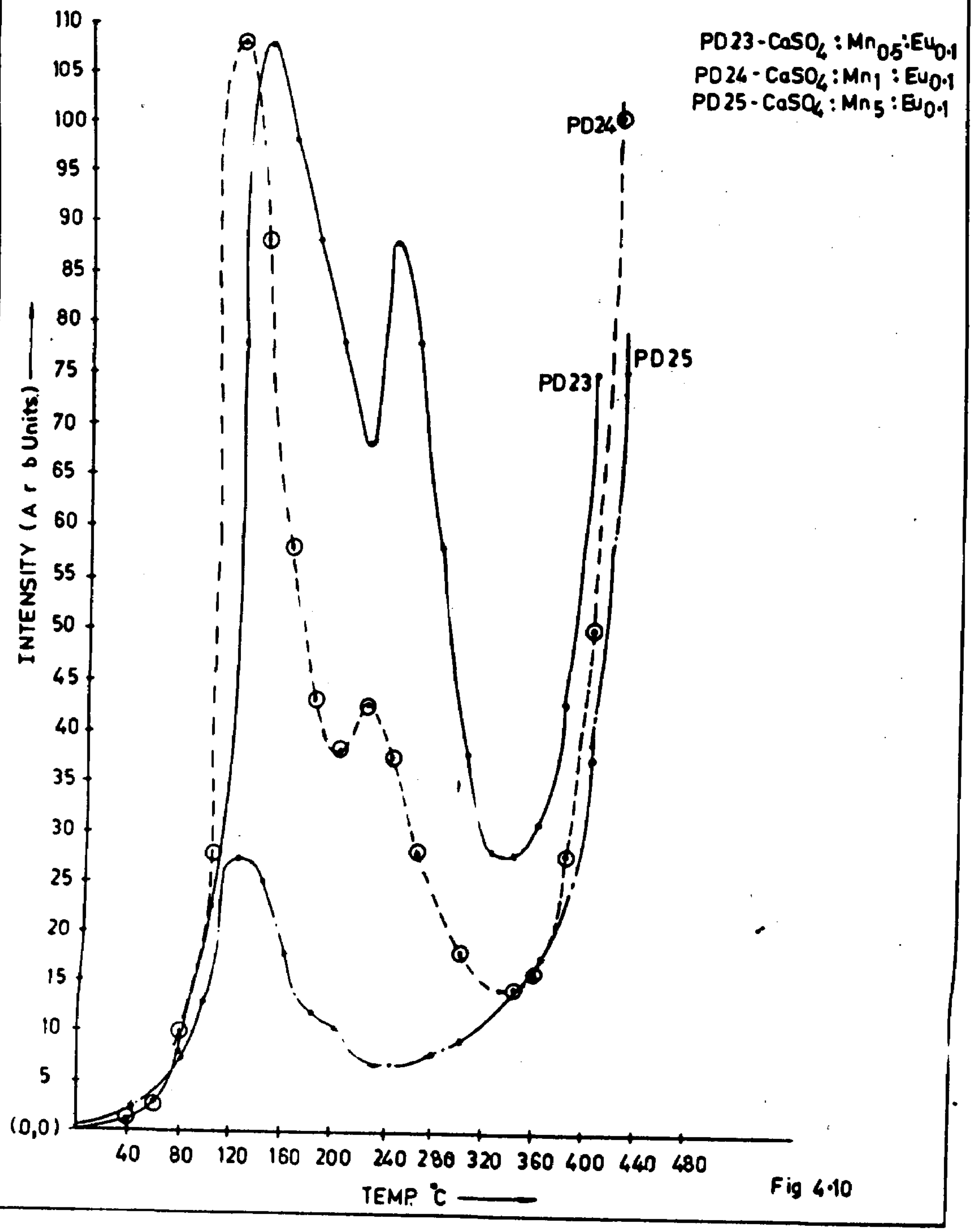


Fig 4·10

TL GLOW CURVES OF CaSO$_4$:Mn:Eu PHOSPHORS OF DIFFERENT CONCENTRATION UNDER GAMMA EXCITATION.

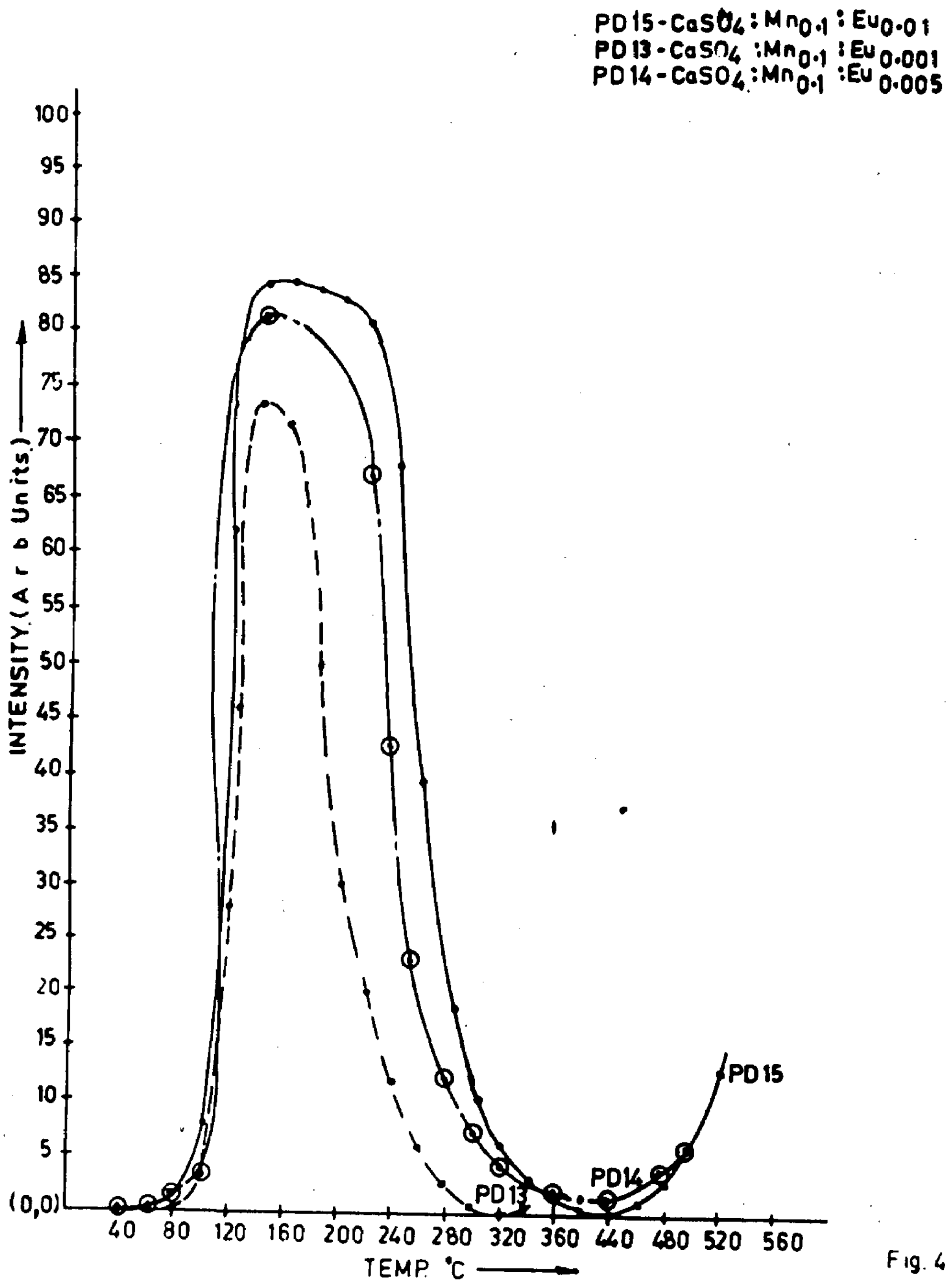


Fig. 4.11

TL GLOW CURVES OF $CaSO_4$:Mn:Eu PHOSPHOR OF DIFFERENT CONCENTRATION UNDER GAMMA EXCITATION.

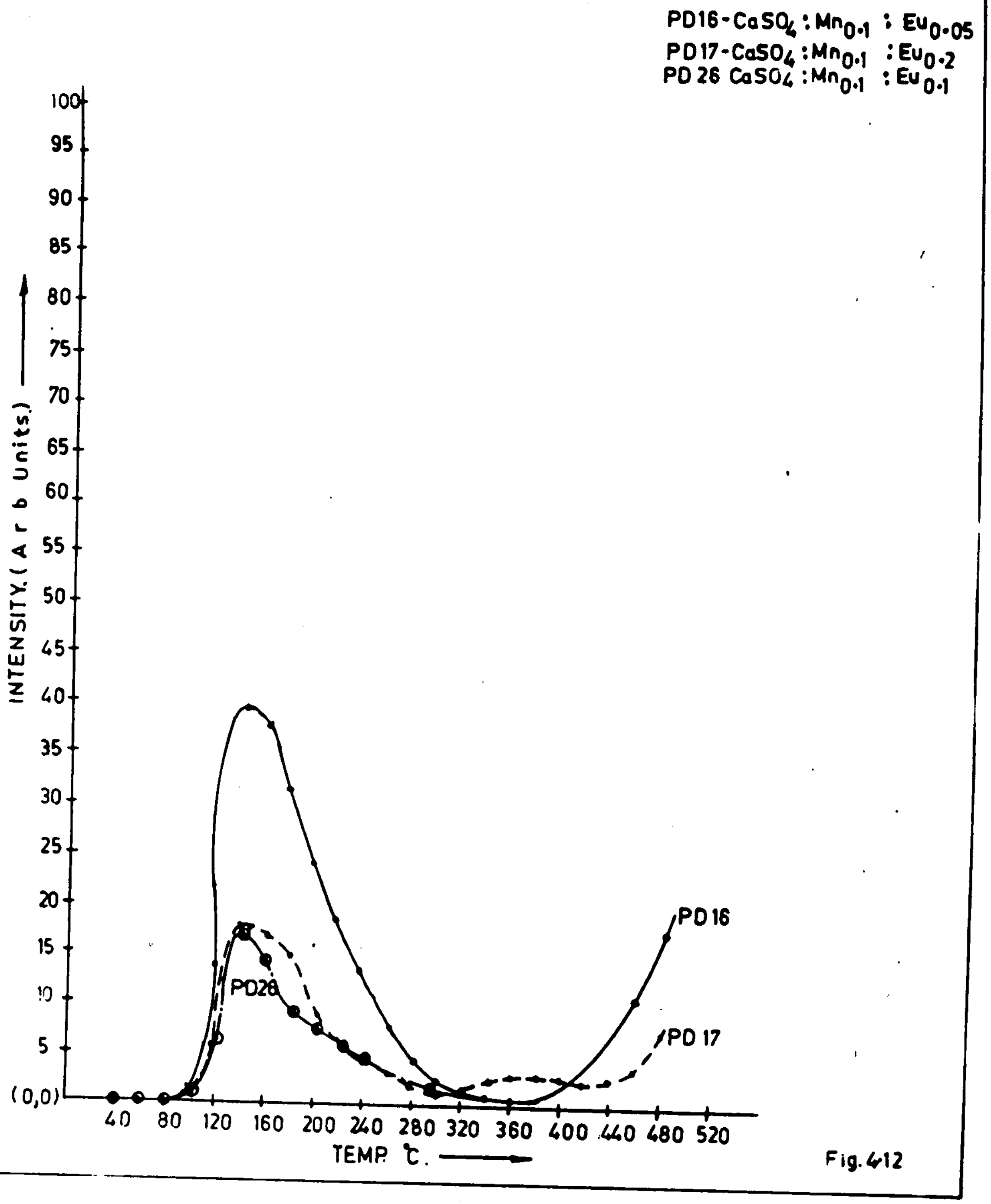
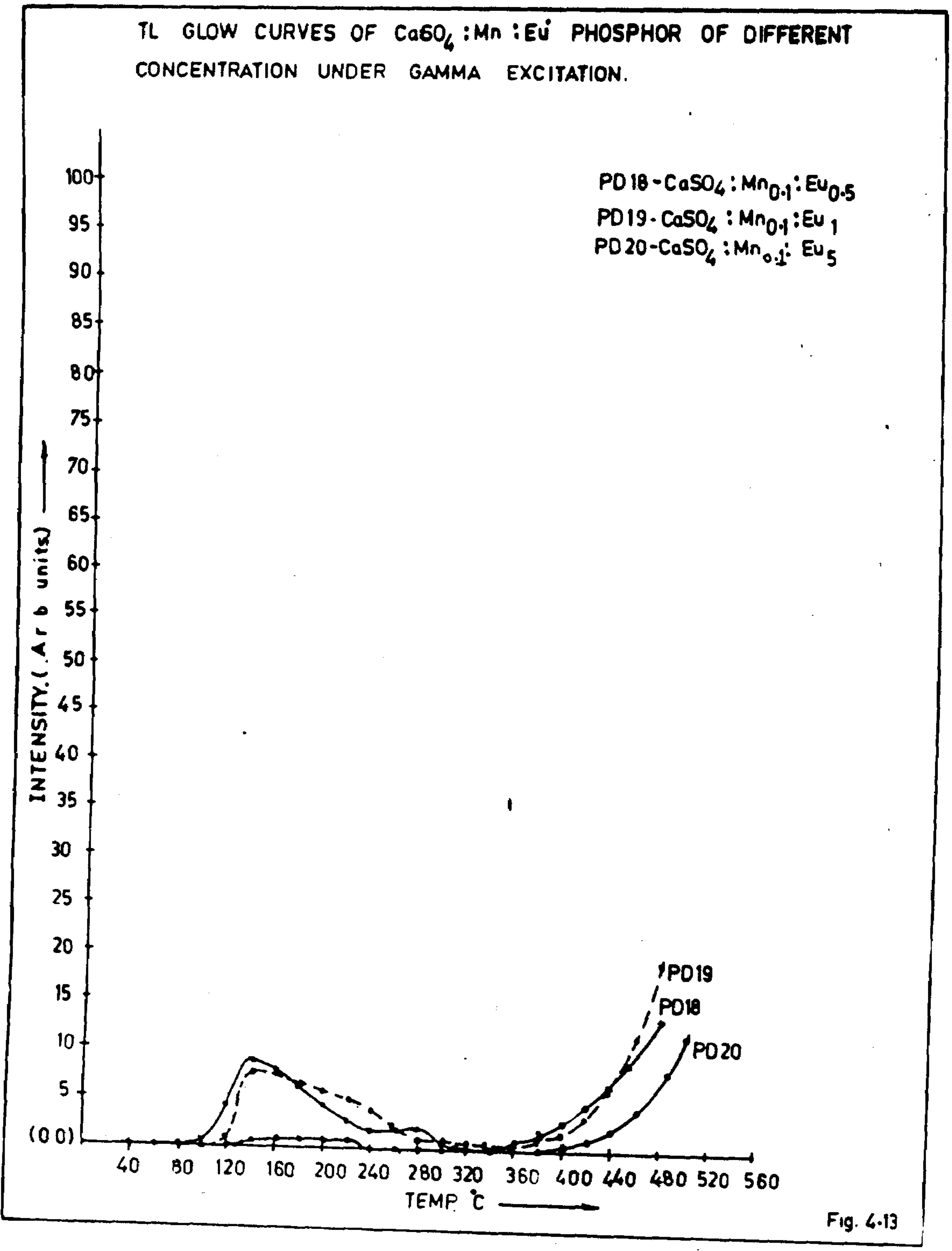
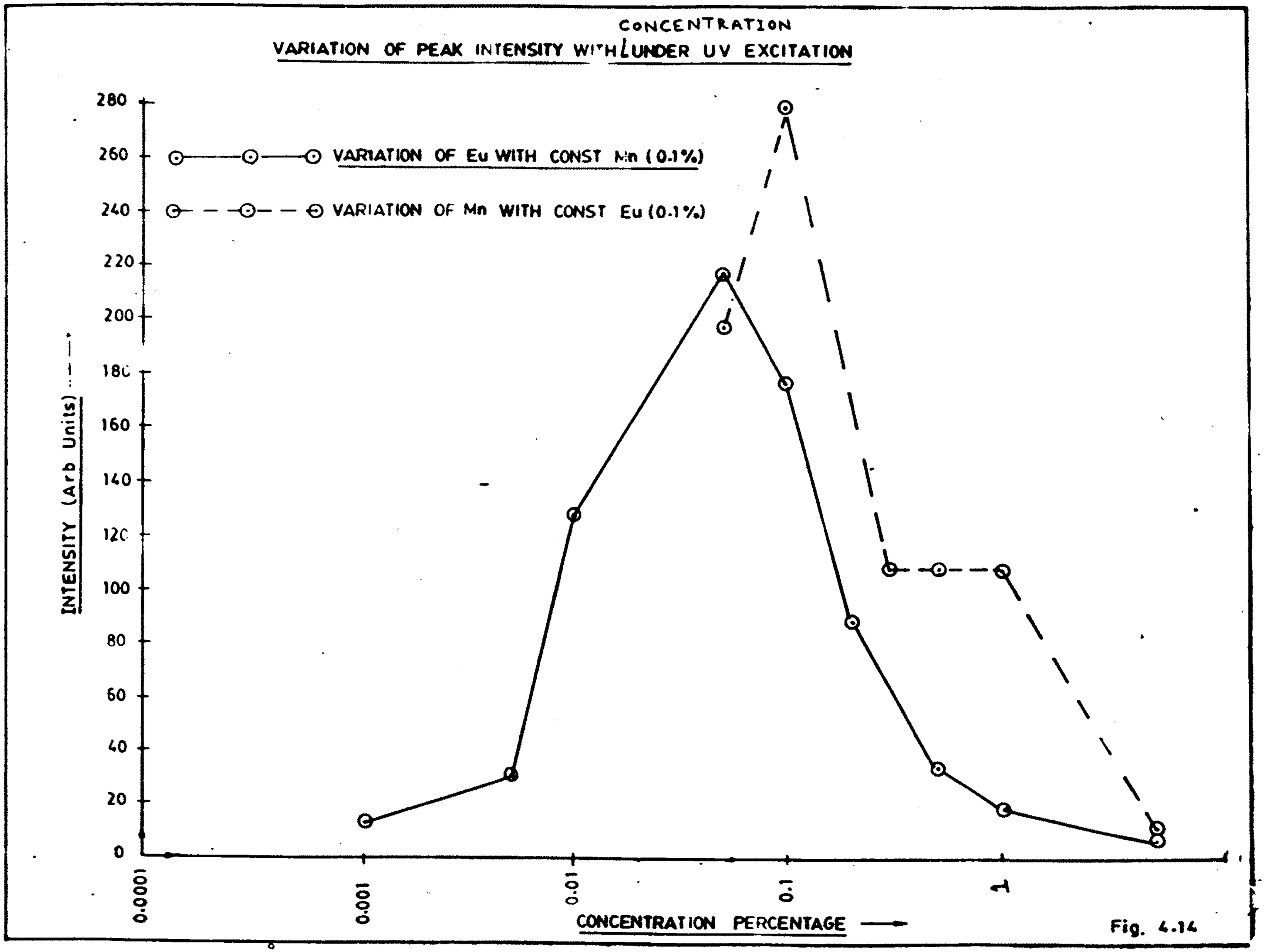


Fig.4.12



TL GLOW CURVES OF $CaSO_4$:Mn :Eu PHOSPHOR OF DIFFERENT CONCENTRATION UNDER GAMMA EXCITATION.

Fig. 4-13



VARIATION OF PEAK INTENSITY WITH CONCENTRATION UNDER UV EXCITATION

Fig. 4.14

VARIATION OF PEAK INTENSITY WITH CONCENTRATION UNDER GAMMA EXCITATION

VARIATION OF Eu WITH CONST Mn (0.1%)

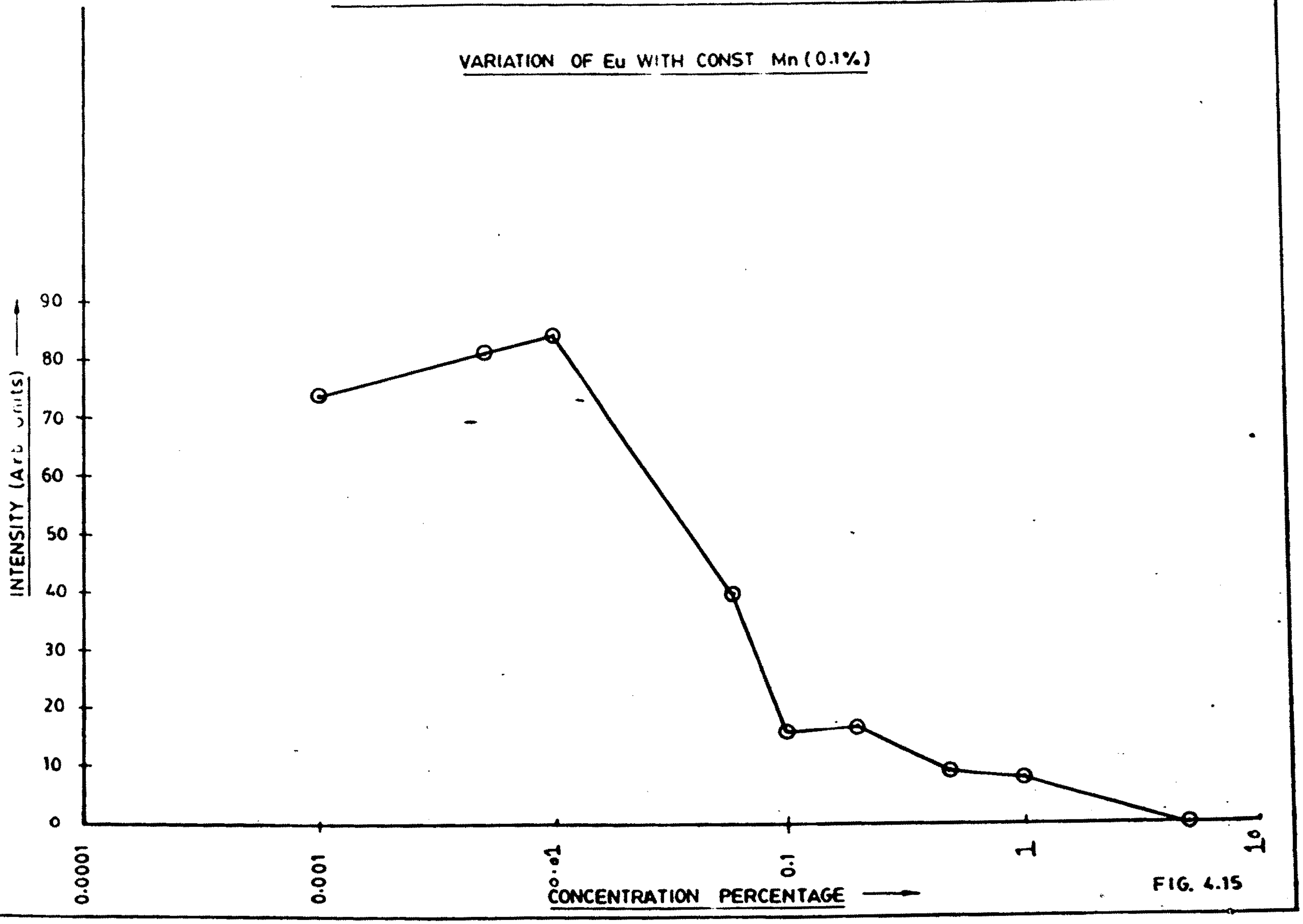


FIG. 4.15

ARRHENIUS PLOTS.(INITIAL RISE METHOD.)
PD12 UNDER UU EXCITATION.

PD12 - $CaSO_4 : Mn_{0.1} : Eu_{0.1}$

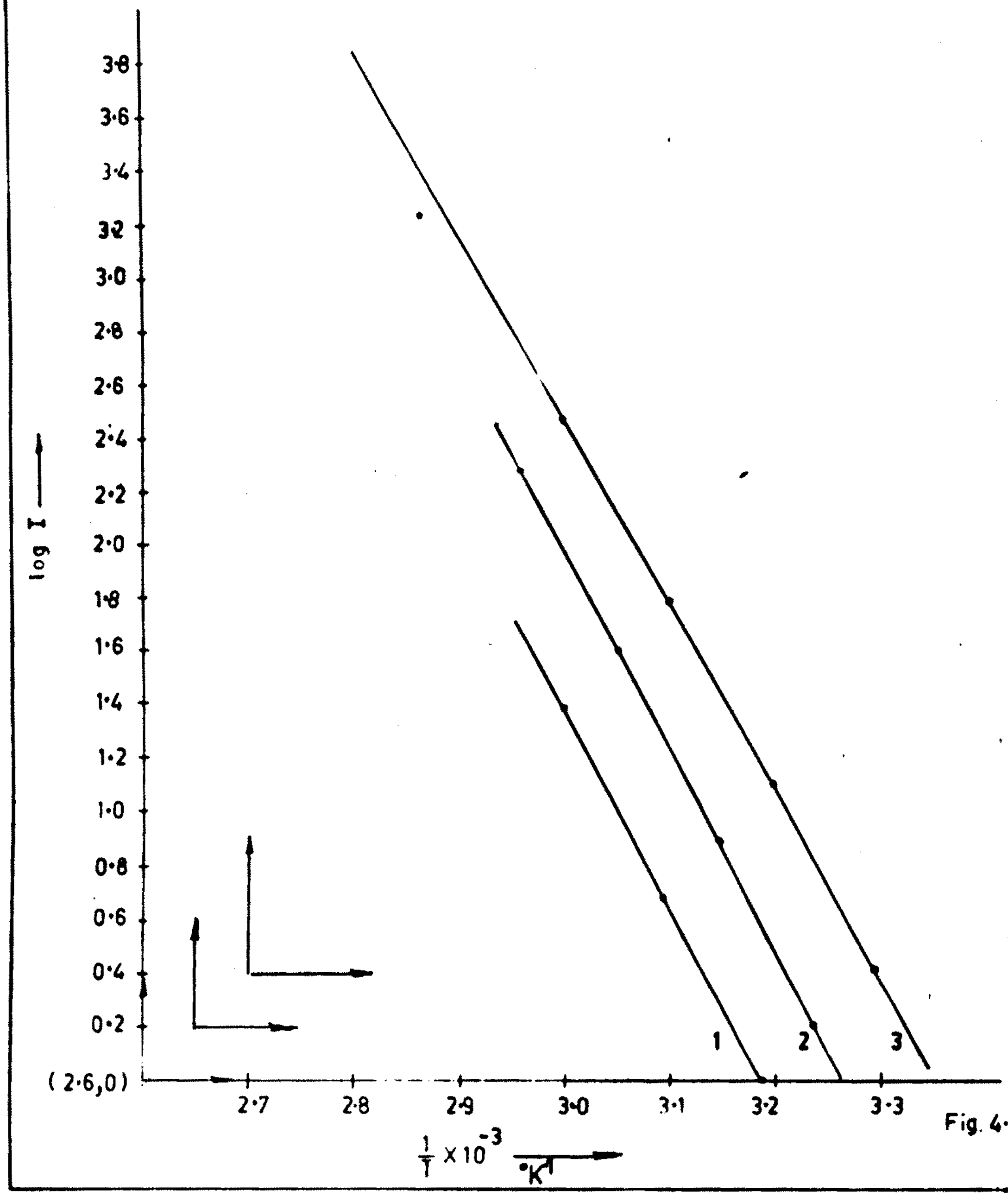


Fig. 4·16

TL GLOW CURVES OF PD 12 PHOSPHOR FOR DIFFERENT TIME OF EXCITATION UNDER UV IRRADIATION

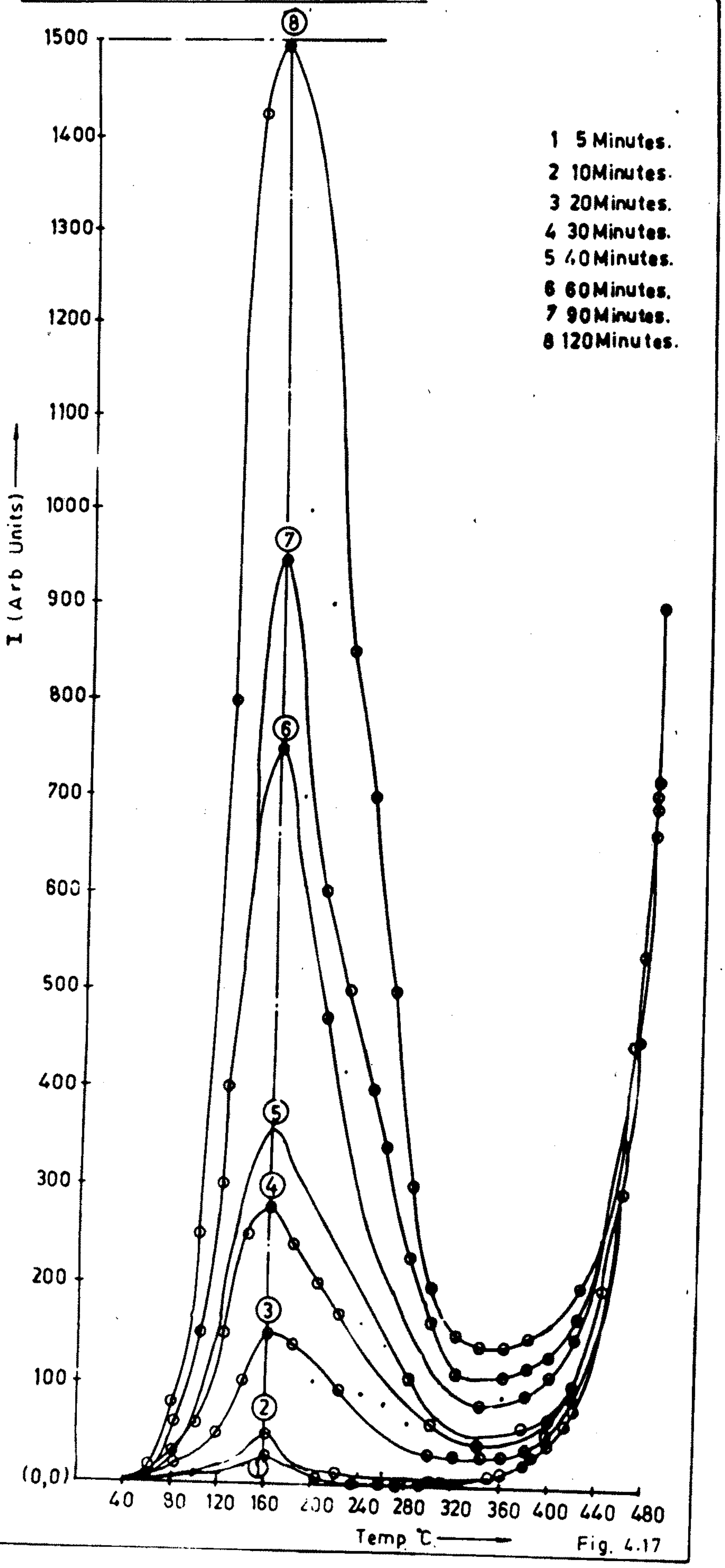


Fig. 4.17

DOSE DEPENDANCE FOR PD 12 PHOSPHOR UNDER UV EXCITATION

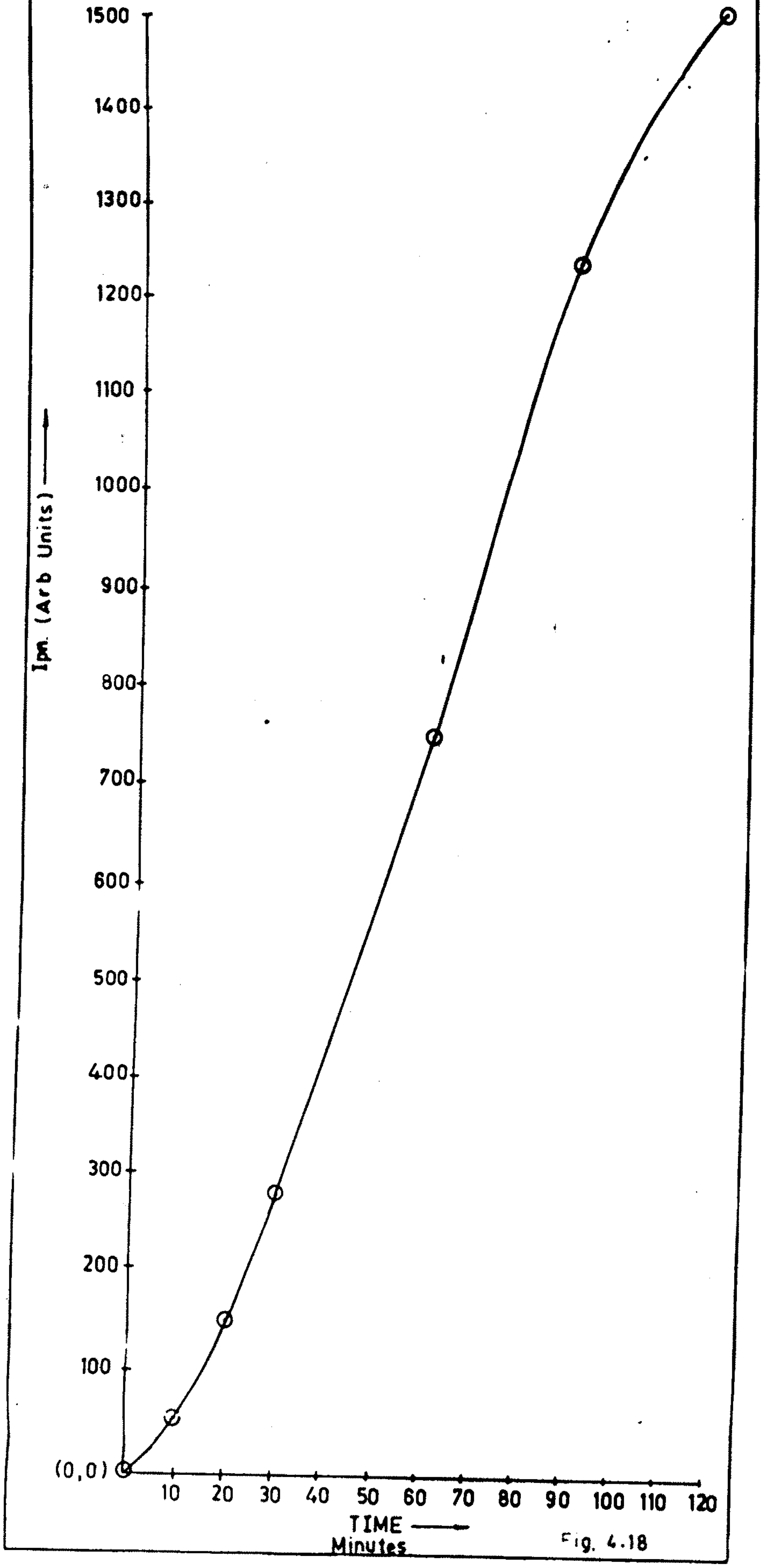


Fig. 4.18

TL GLOW CURVES OF PHOSPHOR PD 12 FOR DIFFERENT TIME OF EXCITATION UNDER GAMMA IRRADIATION

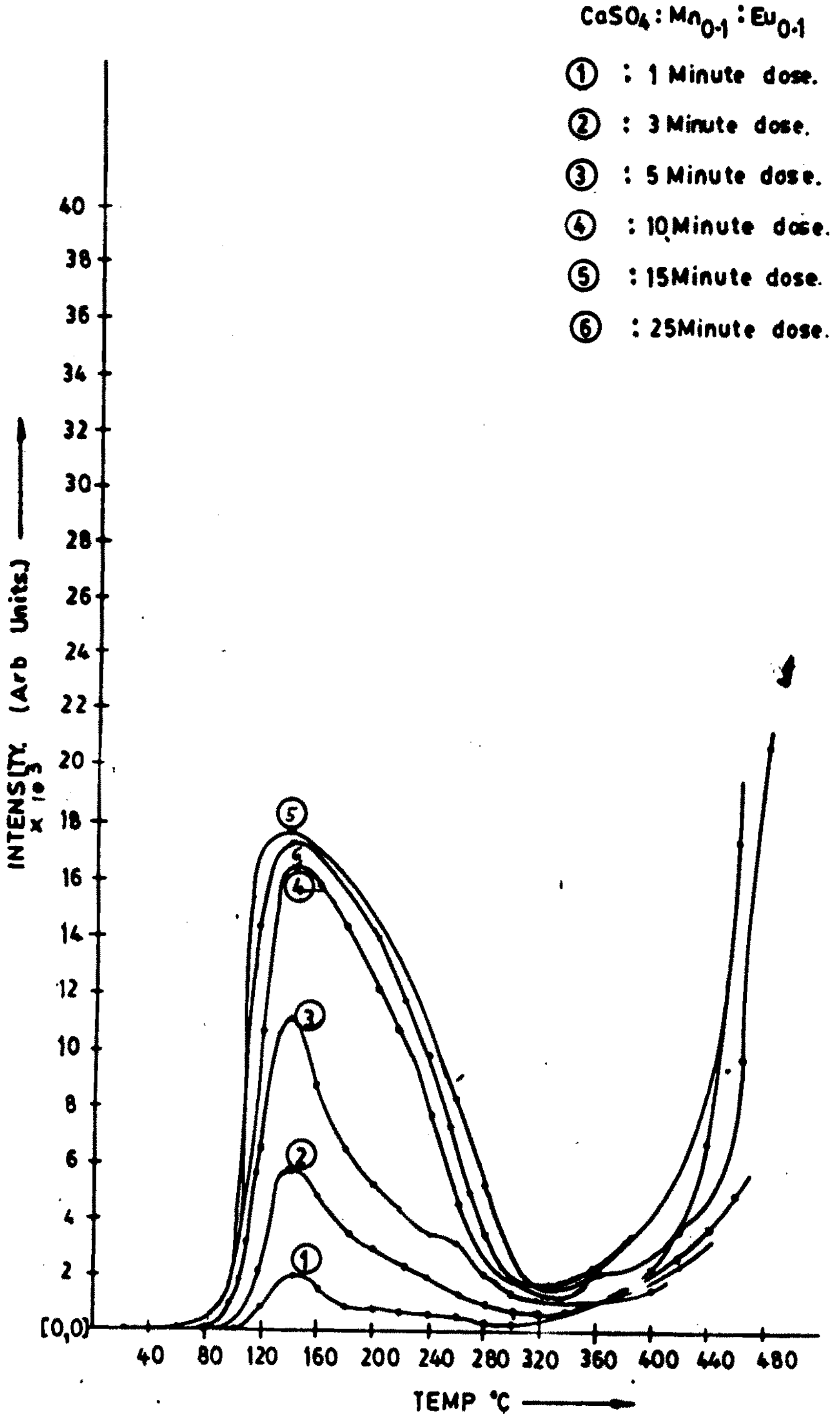


Fig. 4.19

DOSE DEPENDANCE FOR PD12 PHOSPHOR UNDER GAMMA IRRADIATION

PD12: $CaSO_4:Mn_{0.1}:Eu_{0.1}$

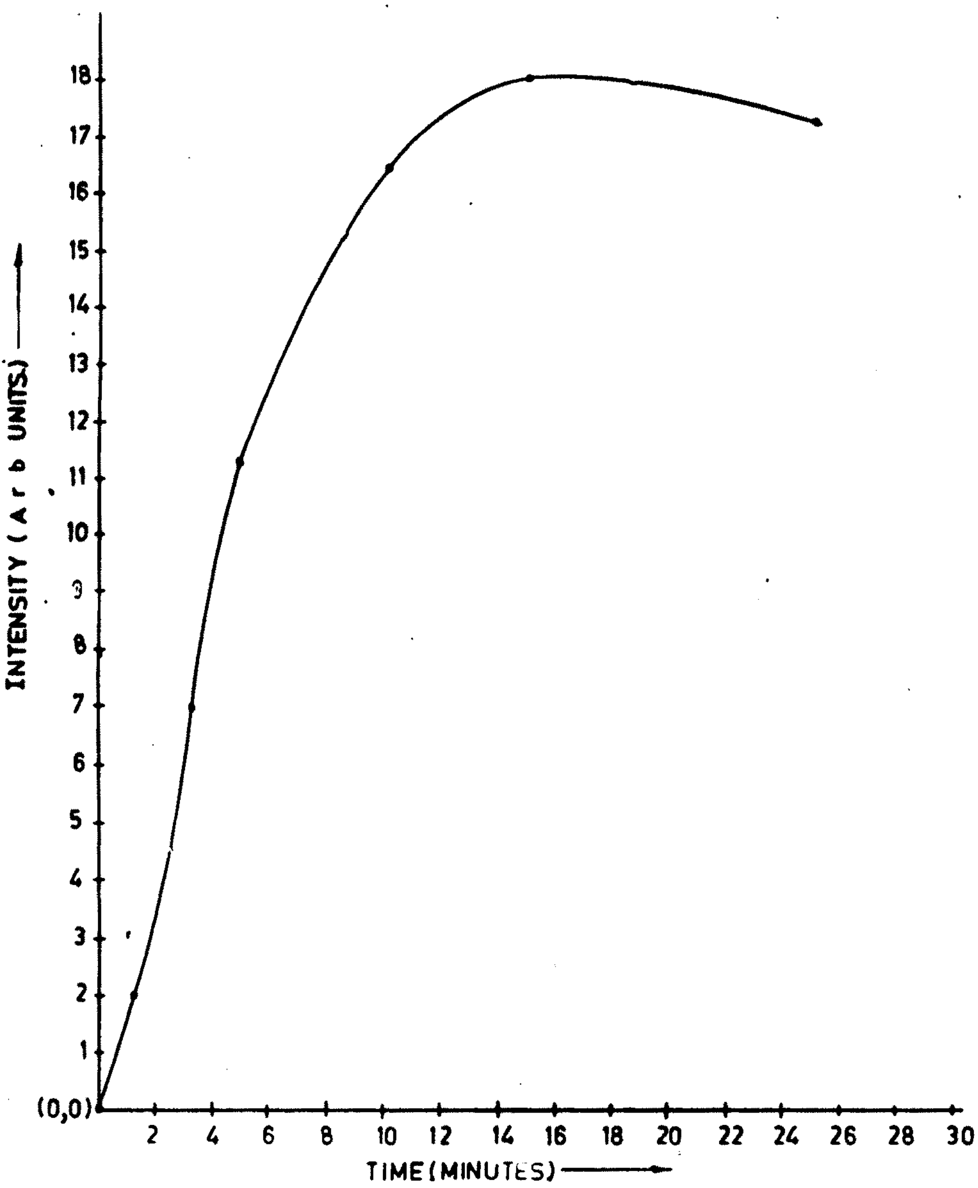


Fig. 4·2