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. In thermoluminescence, on supplying thermal energy, the energy stored in a suitably excited phosphor is released in the form of luminescent emission. The intensity of the luminescent emission is to be measured as a function of temperature. A plot of intensity against temperature is called as glow curve. It can be used for the estimation of activation energy E and escape frequency factor. As both E and S depend sensitively upon the trapping centers, glow curve can yield valuable information above 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 and Sm so as to get the following information :

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 dependance of TL glow peak.

4.2 Theory of Glow Curve

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 (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 -

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

so that, TL intensity is given by

$$I_t \propto n_t \cdot p \qquad .. (4.2)$$

where T = absolute temperature

k = Boltzmann's constant

E = trap depth or activation energy

s = constant having the dimension of frequency

n_t = number of filled traps at time 't'

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

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

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

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

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 walls and the wall reflection coefficient. It then follows that 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 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 (2) have given a simplest mathematical representation for the luminescence glow peaks without any overlaping. The basic assumptions made was

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 occures. 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

$$\begin{aligned} I &= - C \frac{dn}{dt} \\ &= - C P n \\ &= -C n s e^{-E/KT} \qquad .. (4.5) \end{aligned}$$

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

$$\therefore \quad \frac{dn}{n} = - c\, s\, e^{-E/KT} \quad \frac{dt}{dT} \quad dT$$

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

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

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

$$I = n_o\, c\, s\, e^{-E/KT} \exp. \left[- \int_o^T \frac{s}{\beta} \quad e^{-E/KT'} dT' \right] .. (4.7)$$

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 temperature.

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

$$\frac{\beta E}{K\, Tm^2} = s\, e^{-E/KTm} \qquad .. (4.8)$$

At a fixed temperature T, csexp (-E/KT) is a constant, say A. Equation (4.5) can thus be written as

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

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

from equation (4.5) and (4.8)

$$I = I_o\, e^{-At} \text{ where } I_o = An_o \qquad .. (4.10)$$

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 (4) extended 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 released carrier will go to the recombination center is

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

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

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

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

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

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

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

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

where $A' = c\,s'\,e^{-E/KT}$

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.(4.2) 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 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 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 electron in trap at E_1
n_2 = concentration of electron in trap at E_2
n_c = concentration of electrons in the conduction band
n_v = concentration of holes in the valence 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. (4.2)

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

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

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

The charge balance gives

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

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

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

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 function of temp. when linear heating program $\beta = t$ is used.

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

which reduces when N_2 is neglgible to

$$(1 - f) \ln x + \frac{f}{Y}\left(1 - \frac{1}{x}\right) + \frac{S}{\beta} \int_{T_o}^{T} e^{-E/KT'}\, dT' = 0 \quad ..(4.1$$

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 thermoluminescnece intensity, I, for model-I given by

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

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 $f = 0$ & $f = 1$ respt.

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

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

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

while applying model I of the above approach to determine the TL parameters, Braunlich (8) and Shenkar and Chen (7) showed the dependance of the obtained values on the trap occupancy. Shenkar and Chen in particularly demonstrated by computation that the term 'kinetics order' may become meaning less if the inequality

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

$$RN_3 < q \, (N_1 - n_1)$$

changes direction during the TL glow peak emission.

4.3 Methods for determining trap depth :

There exists 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. 4.1 represent a general shape of glow curve defining some characteristic quantities such as Tm, 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 to that of luminescence centrers. 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 (10) showed that the activation energy for the first order kinetics is given by

$$E = \frac{K\,Tm^2}{T_2 - Tm} \qquad .. (4.23)$$

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

$$E = \frac{2\,kTm^2}{T_2 - Tm} \qquad .. (4.24)$$

In the above equations Tm 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 kinetics respectively. Thus we have

$$E = 0.976\,\frac{KTm^2}{T_2 - Tm} \qquad .. (4.25)$$ for first order kinetics

and $$E = 1.706\,\frac{K\,Tm^2}{T_2 - Tm} \qquad .. (4.26)$$ 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 (12,13) considered the luminescence emission as mainly due to two kinds of recombination process. In one process (sub model I of fig. 4.2) 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. 4.2). 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	$E_1 = \frac{KTm^2}{T_2 - Tm}$	$\mu_g \simeq e^{-1}$ ..(4.27)
b) Retrapping dominant	$E_2 = \frac{2\,KTm^2}{T_2 - Tm}$	$\mu_g \simeq 0.5$ ..(4.28)
via conduction band	$\varrho \simeq 1$	
a) First order Kinetics dominant	$E_3 = \frac{1.72\,K\,Tm^2}{(Tm - T_1)}\left(1 - \frac{5.16}{\Delta}\right)$	$\mu_g \leqslant e^{-1}\left(1 + \frac{2}{\Delta}\right)$ ..(4.29)
b) second order Kinetics dominant	$E_4 = \frac{2K\,Tm2}{Tm - T_1}\left(1 - \frac{6}{\Delta}\right)$	$\mu_g \geqslant e^{-1}\left(1 + \frac{2}{\Delta}\right)$ ..(4.30)

where $\frac{1}{\Delta} = \frac{KTm}{E} << 1$ 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.

The factor $\mu_g = \frac{\delta}{W} = \frac{T_2 - Tm}{T_2 - T_1}$

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

$\mu g \leq e^{-1}(1 + 2/\Delta)$ for first order kinetics

& $\mu g > e^{-1}(1 + 2/\Delta)$ 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 temperature side of glow peak causes an apparent increase in the μg values which may wrongly indicate the proces 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 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

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

with coddition $\mu g = 0.5$

Chen (11) has modified these formulae to avoid the interaction and gave following equations. For first order Kinetics,

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

and for second order kinetics,

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

c) <u>Method using full half width of the glow peak</u> :

(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 gave following relations.

For first order Kinetics

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

and for second order kinetics

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

Here numerical constants are choosen emperically to have a better estimation of E and $\frac{E}{K\,Tm} >> 1$. Moreover Chen (15) showed that the symmetry factor $\mu g = 0.42$ is characteristic of first-order peaks and $\mu g = 0.52$ that of second order. On correlating the symmetry factor μg and order of kinetics α, he gave the following equations to evaluate E for general order kinetics.

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

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

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

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 independantly 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 temperature at two different heating rates β_1 and β_2. Eliminating s from equation.

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

they found

$$E = \frac{K\,Tm_1\,Tm_2}{Tm_1 - Tm_2}\ \mathrm{Ln}\ \frac{\beta_1\,Tm_2^2}{\beta_2\,T_{m_1}^2} \qquad ..\ (4.39)$$

If Tm can be measured within an accuracy of $1^{\circ}K$, the method is found to yield E within an error of 5% (19).

b) Method due to Schon :

To achive an improved accuracy in E values Schon (20) modified the eq^{n}. (4.39) by replacing Tm^2 by $Tm^{3.5}$ which results in

$$E = \frac{K\, Tm_1\, Tm_2}{Tm_1 - Tm_2} \quad Ln \frac{\beta_1 \; Tm_2^{3.5}}{\beta_2 \; Tm_1^{3.5}} \qquad \text{----} \quad (4.40)$$

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 (21) have shown a plot of Ln ($Imi\, Tm_i^4/\beta i^2$) versus (1/Tmi). 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

$$Ln \frac{Tm_i^2}{\beta i} = \frac{E}{KT_{mi}} + Ln \frac{E}{SK} \qquad \text{----} \quad (4.41)$$

Thus the plot between Ln ($Tm_i^2/\beta i$) and (1/Tmi) 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 $S = 10^{0}$ sec^{-1}. The equation is

$$E = Tm/500 \qquad \text{----} \quad (4.42)$$

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

$$S \exp. \left(-E/KT_m \right) \left(1 + f(S,\beta)\right) = 1 \qquad \text{---- (4.43)}$$

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

$$E = T_m \left(1 + f(S,\beta)\right) K \log s \qquad \text{---- (4.44)}$$

where $f(S,\beta)$ is another function of S and β. When β lies between 0.5 and 2.5^{o} K sec^{-1} and S equals the value 2.9×10^{9} sec^{-1}, the above equation reduces to

$$E = 25\ k\ T_m \qquad \text{---- (4.45)}$$

c) <u>Method due to Grosswiner</u> :

Grosswiner (24) derived an equation for determining E_1 for first order kinetics as

$$E = \frac{1.51\ k\ T_m T_1}{T_m - T_1} \qquad \text{---- (4.46)}$$

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

Chen's modification to Grosswiner :

Chen modified the Grosswiner's relation emperically giving

$$E = \frac{C_1\ KT_m\ T_1}{T_m - T_1} \qquad \text{---- (4.47)}$$

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 about 7% higher for an improved accuracy they suggested emperically

$$E = C_8 \frac{K\,Tm\,T_1}{(T_m - T_1)} \qquad \text{---- (4.48)}$$

According to them when $E/K\,Tm$ = 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& 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

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

F 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 the initial part of glow curve the equation (4.49) takes the form

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

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 assending 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 & Ganguly :

Activation energy can be determined by the 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

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

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 non isothermal conditions are avoided. The decay curve obtained cam be analysed in to sum of sharply defined linear region and it has been shown (28) that for the first order kinetics

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

where t is time

Taking logarithm of equation (4.52) we have

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

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

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

Taking the slopes m1 and m2 at two different temperatures T1 and T2 one can write

$$\log \frac{m_1}{m_2} = \frac{E}{K} \left(\frac{1}{T_1} - \frac{1}{T_2} \right) \quad \text{.----(4.55)}$$

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

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

4.4.1 Method due to Randall and Wilkins

Randall & Wilkins (2) for the 1st order kinetics have given the general equation.

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

$$I = S_{no} \exp.(-E/KT) \exp.\left[- \frac{S}{\beta} \int_{T}^{T_o} \exp.(-E/KT')\, dT' \right] \quad .. \ (4.56)$$

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

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

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 Method due to Garlick and Gibson

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

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

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

$$1 + \frac{S' n_o}{\beta} \int_{T_o}^{Tm} \exp.(-E/KT)\, dT.$$
$$= 2 \frac{k T^2 m}{\beta E} S' n_o \exp.(-E/KT_m) \quad .. \ (4.59)$$

Assuming T_m to be the experimental peak temp. 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 points that in an isothermal decay a plot of log I verssues t may be regarded as a sum of sharply defined linear region slope m given by the equation. $m = s \exp.(-E/KT)$. By knowing E, the frequency factor s can be calculated using equation.

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

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,

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

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 center is equal to the trapped electron concentration.

4.4.5 Method due to Curie

As suggested by Curie (30), the glow peak temp.T_m and heating rate β are related to escape frequency factor, by the equation of the type.

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

where $\delta = T_2 - T_m$ is high temp. half width. Once 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 traping centre can be evaluated from the knowledge of escape frequency factor.

Mott and Gurney (31) 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.

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

on combining this equation with equation viz.

$$p = \frac{1}{\tau} = S\ \exp.(-E/kT)$$

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

4.6.1 Results obtained when samples were excited by uv source for three minutes.

A) Glow Curves

TL glow curves are plotted for undoped CaS and CaS with Mn and Sm as activators (fig. 4.6). The heating rate used was 2°k/sec. The measurements have been carried out in the temperature range of 300°k to 573°k. Fig. 4.3 shows the temperature profile of the linear temperature programmer. From these plots it seems that undoped CaS exhibits very weak luminescence. This luminescnece may be due to defects in the crystal structure or inherent impurities present in the starting material. The luminescence gets enhanced in presence of activators Mn and Sm. However, overall shape remain same.

Typical glow curves for various samples with different concentrations of Mn and Sm are shown in fig.4.7 to 4.13. As seen from the graphs a single broad peak at around 393°K is observed for all phosphors. From the shape of glow curves it seems that the peak temperature slightely changes with concentration of activator Mn and second activator Sm. The shift in peak temperature indicates that, instead of having a single peak at around 393°k, the samples 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 the peak to be single.

It is observed that overall shape of the glow curve is not significantly affected by variation of concentration of Mn and Sm. Only the peak intensity changes with concentration fig. 4.14 shows the variation of peak intensity with concentration of Mn and Sm. From this graph it is seen that peak intensity initially increases and then decreases with the concentration of Mn and Sm. The variation of peak temperature and peak intensity is given in table 4.1.

As such from TL point of view, the phosphor SD 12 with composition $CaS:Mn_{0\cdot05}:Sm_{0\cdot02}$ gives maximum TLoutput amongst the choosen concentration. Thus the optimum concentration of Mn in the host seems to be around 0.05% and for Sm it is around 0.02%

B) Activation energy

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 shape of glow curve by using methods due to (i) Urbach (ii) Luschik, iii) Halperin and Braner, (iv) Chen, (v) Grossweiner. Values thus calculated by different formulae are listed in table 4.2, and are in good agreement.

An attempt is also made to find the activation energy by initial rise method for sample SD 14. Typical Arrhenius plots are shown in fig.4.15. The activation energy calculated by this method is 1.053 eV.

C) Variation of activation energy with activator concentration :

It is seen from table 4.2 that activation energy does not vary significantly with activator concentration. The effective trap levels are distributed from 0.4 eV to 0.9 eV. The 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 thermoluminescence (33, 34).

D) Kinetics of luminescence

The 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 μg for present glow peaks are listed in table 4.2. For some samples the values are less than $e^{-1}(1 + \frac{2}{\Delta})$ and for others, the values are greater. This may be due to the composite nature of the glow peak instead of a single peak. Hence any conclusion about the kinetics, drawn from the magnitude of μ_g is likely to be erroneous. Efforts are therefore made to determine kinetics by another method.

Plots of log I versus t in an isothermal decay are not straight line (fig. 4.16) indicating that kinetics is not first order (monomolecular). However, plots of $1/\sqrt{I}$ versus time (in isothermal decay) are straight line (fig. 4.17) which suggests that order of kinetics may be second order (bimolecular process).

F) Escape frequency factor

The escape frequency factor 'S' is calculated by using equation (4.8). The values of 'S' obtained are mainly dependent on E . The 's' values are estimated by taking activation energies calculated from Luschik formula and Urbach formula. They are listed in table 4.3. The s values vary from 10^6 sec^{-1} to 10^{12} sec^{-1}.

G) Size of traps

The capture cross section (σ) of each type of trapping center 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 4.3. The size of trap is about 10^{-18} cm^2. The trap in the present investigation may be regarded as medium size trap (35).

H) Dose dependance

The peak intensity of a glow curve is found to be a function of excitation dose. The glow curves for various excitation time are shown in fig. 4.18 and the plot of glow peak intensity versus duration of excitation are shown in fig 4.19 for a sample SD 14. The peak intensity of a glow curve initially increases gradually and then saturates around a uv excitation of 45 minutes.

4.6.2 Results obtained when excitation source used is Co60 gamma source. (Dose of 4000 R/minute for 30 minutes)

A) Glow Curves :

The TL glow curves of the sample excited by gamma irradiation (4000 R/minute for 30 minutes) are shown in fig. 4.20 to 4.24. The heating rate used is 2°k/sec. The measurements have been carried out in the temperature range of 300°k to 573°k. The glow curves are recorded 92 days after gamma irradiation. All the glow curves exhibit two peaks, first around 423°k (weak) and second around 475°k (strong). Peak around 393°k observed in u.v. excited phosphors is missing which is probably due to room temp. decay of low temp. peak(37). The high temperature peak in gamma irradiated phosphors which is not observed in uv excited samples may be probably due to high energy irradiation creating deep traps which favour high temp. peak. The observation however requires persual.

The peak temperature is almost constant with activators concentration variation. The peak intensity changes with activator concentration (table 4.4). However the change is not systematic. Since decay correction is not applied, it is difficult to arrive at a systematic conclusion regarding concentration variation and TL output.

It was confirmed by following procedure that gamma irradiation does not cause radiation damage in phosphors. After recording TL glow curve of gamma irradiated sample, the same sample was uv excited and its TL was recorded. The shape of glow curve, peak temperature and peak intensity remains unaffected

B) Activation energies

In the present study activation energies (for peak around 475°k) are calculated by Urbach formula. Table 4.4 shows the calculated activation energies. It seems from the table 4.4 that activation energies are almost constant with concentration variation.

C) Kinetics of Luminescence

The kinetics involved in thermoluminescence is determined by calculating the values of symmetry factor μ . It is observed that μ is greater than $\frac{1}{e}$ (table 4.4) which indicates that order of kinetics may be second order.

D) Escape Frequency factor

The escape frequency factor 's' is evaluated by using equation (4.8). The values of 's' calculated are listed in table 4.4 and are of the order of 10^{9} sec^{-1} for variation in activator concentration.

E) Size of trap

The size of trap is calculated by using equation 4.64. The values are listed in table (4.4). The size of the trap is of the order of $10^{-18} cm^{2}$. The traps may be regarded as medium size trap.

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. However, the peak intensities are significantly influenced by activators (Mn & Sm).

2) Addition of activators does not give rise to new glow peaks in the temperature region studied.

3) Trap depths of effective levels are insensitive to the concentration of activators (Mn, Sm).

4) The probable kinetics involved in thermoluminescence process is likely to be second order (Bimolcular).

5) The glow peak intensity is a function of excitation time.

Table No.4.1 : Observation table showing the peak temperature & peak intensity values obtained from glow curves of uv excited samples.

Sample no.	Peak Temp. ^oK	Peak intensity nA
SD 12	379	1150
SD 13	389	2500
SD 14	395	2100
SD 15	395	810
SD 16	393	1120
SD 17	395	1200
SD 18	393	185
SD 19	399	79
SD 20	399	59
SD 21	393	625
SD 22	393	1200
SD 23	385	1650
SD 24	393	760
SD 25	391	765
SD 26	393	630
SD 27	397	605
SD 28	389	695

Table 4.2 : Showing activation Energy calculated with different formulae (UV excited samples).

E_U - Energy calculated from Urbach formula

E_{LC} - Energy calculated from Luschik formula with Chen's correction.

E_{HBC} - Energy calculated from Halperin & Braner formula with Chen's correction.

E_C - Energy calculated from Chen's formula

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

Sample no.	E_U	E_{LC}	E_{HBC}	E_C	E_{GC}	μ
SD 12	0.758	0.587	0.4951	0.4785	0.4181	0.45
SD 13	0.778	0.9276	0.3631	0.5360	0.3653	0.31578
SD 14	0.79	0.8564	0.3837	0.5377	0.3593	0.30769
SD 15	0.79	0.8198	0.5127	0.6070	0.4810	0.4
SD 16	0.786	0.8742	0.6423	0.7119	0.6012	0.433
SD 17	0.790	0.8198	0.4199	0.5377	0.3949	0.3589
SD 18	0.786	0.8738	0.3966	0.6202	0.3734	0.3333
SD 19	0.798	0.7322	0.3209	0.4334	0.3026	0.3333
SD 20	0.798	0.9010	0.6642	0.7348	0.6206	0.4333
SD 21	0.786	0.8116	0.5685	0.6410	0.5319	0.4242
SD 22	0.786	0.8116	0.4432	0.5478	0.4092	0.3684
SD 23	0.77	0.8386	0.5768	0.6577	0.5408	0.4193
SD 24	0.786	0.9468	0.4258	0.5730	0.3996	0.3287
SD 25	0.782	1.022	0.4763	0.6342	0.4468	0.3333
SD 26	0.756	1.42	0.7955	0.946	0.7423	0.3636
SD 27	0.794	0.8918	0.5885	0.6774	0.5434	0.4062
SD 28	0.778	0.8562	0.4964	0.6069	0.4656	0.3823

Table 4.3 : Showing frequency factor and size of trap (uv excitation).

Sample no	Frequency factor		Size of trap cm^2
	S_{LC} sec^{-1}	S_U sec^{-1}	
SD 12	5.96×10^{6}	1.44×10^{9}	9.6×10^{-18}
SD 13	1.44×10^{11}	1.40×10^{9}	9.33×10^{-18}
SD 14	2.2×10^{11}	1.38×10^{9}	9.2×10^{-18}
SD 15	3.43×10^{9}	1.38×10^{9}	9.38×10^{-18}
SD 16	2.083×10^{10}	1.39×10^{9}	9.27×10^{-18}
SD 17	3.43×10^{9}	1.38×10^{9}	9.2×10^{-18}
SD 18	2.08×10^{10}	1.39×10^{9}	9.27×10^{-18}
SD 19	1.85×10^{8}	1.37×10^{9}	9.13×10^{-18}
SD 20	3.08×10^{10}	1.37×10^{9}	9.13×10^{-18}
SD 21	3.05×10^{9}	1.39×10^{9}	9.27×10^{-18}
SD 22	3.05×10^{9}	1.39×10^{9}	9.27×10^{-18}
SD 23	1.218×10^{10}	1.41×10^{9}	9.4×10^{-18}
SD 24	1.92×10^{11}	1.39×10^{9}	9.27×10^{-18}
SD 25	1.79×10^{12}	1.4×10^{9}	9.33×10^{-18}
SD 26	3.3×10^{17}	1.39×10^{9}	9.27×10^{-18}
SD 27	2.68×10^{10}	1.37×10^{9}	9.13×10^{-18}
SD 28	1.58×10^{10}	1.4×10^{9}	9.33×10^{-18}

S_{LC} - Escape frequency factor calculated by taking activation energy E_{LC}

S_U - Escape frequency factor calculated by taking activation energy E_U

σ - size of trap calculated by taking S_U.

Table No. 4.4 : showing peak temperature, peak intensity, symmetry factor, activation energy, frequency factor and size of trap for γ irradiated samples

Sample no.	Peak Temp. °K	Peak s Intensity nA	μ	Activation Energy eV	Frequency factor sec-$^{-1}$	Size of trap cm^2
SD 12	196	160	0.57	0.938	1.163×10^9	7.753×10^{-18}
SD 13	206	2200	0.64	0.958	1.139×10^9	7.593×10^{-18}
SD 14	204	700	0.70	0.954	1.1438×10^9	7.625×10^{-18}
SD 16	208	600	0.58	0.962	1.134×10^9	7.50×10^{-18}
SD 17	208	1100	0.75	0.962	1.134×10^9	7.56×10^{-18}
SD 18	206	3300	0.64	0.958	1.139×10^9	7.593×10^{-18}
SD 19	206	1500	0.64	0.958	1.139×10^9	7.593×10^{-18}
SD 20	206	1900	0.70	0.958	1.139×10^9	7.593×10^{-18}
SD 21	202	1250	0.38	0.950	1.486×10^9	7.657×10^{-18}
SD 22	206	2000	0.65	0.958	1.139×10^9	7.593×10^{-18}
SD 24	196	2400	0.45	0.938	1.163×10^9	7.593×10^{-18}
SD 25	190	950	0.58	0.926	1.178×10^9	7.853×10^{-18}
SD 26	208	3900	0.62	0.962	1.134×10^9	7.560×10^{-18}
SD 27	202	2800	0.62	0.950	1.148×10^9	7.857×10^{-18}
SD 28	200	800	0.58	0.946	1.153×10^9	7.686×10^{-18}

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UV EXCITED SAMPLES

GLOW CURVE FOR CaS:Mn:Sm PHOSPHOR

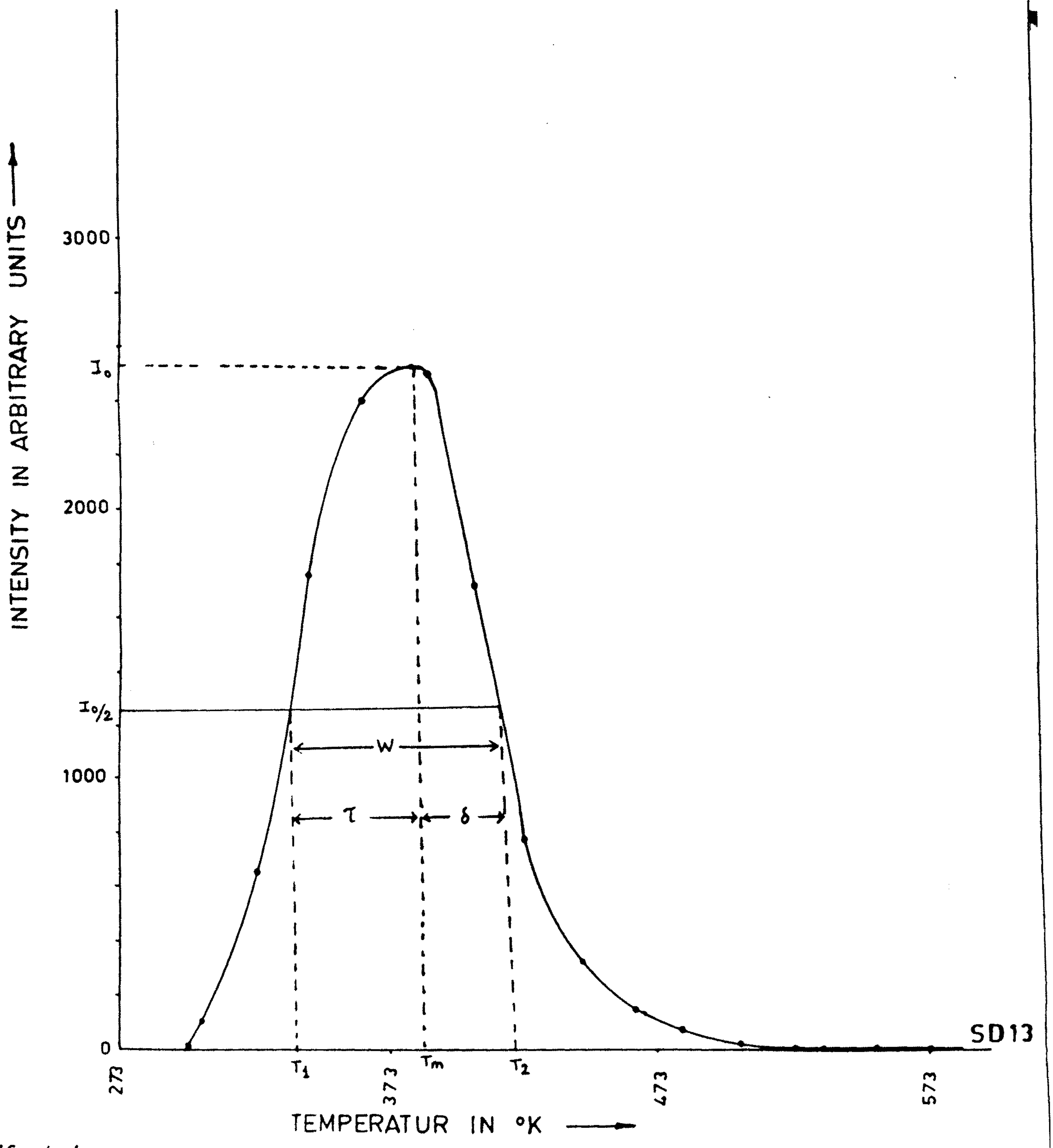
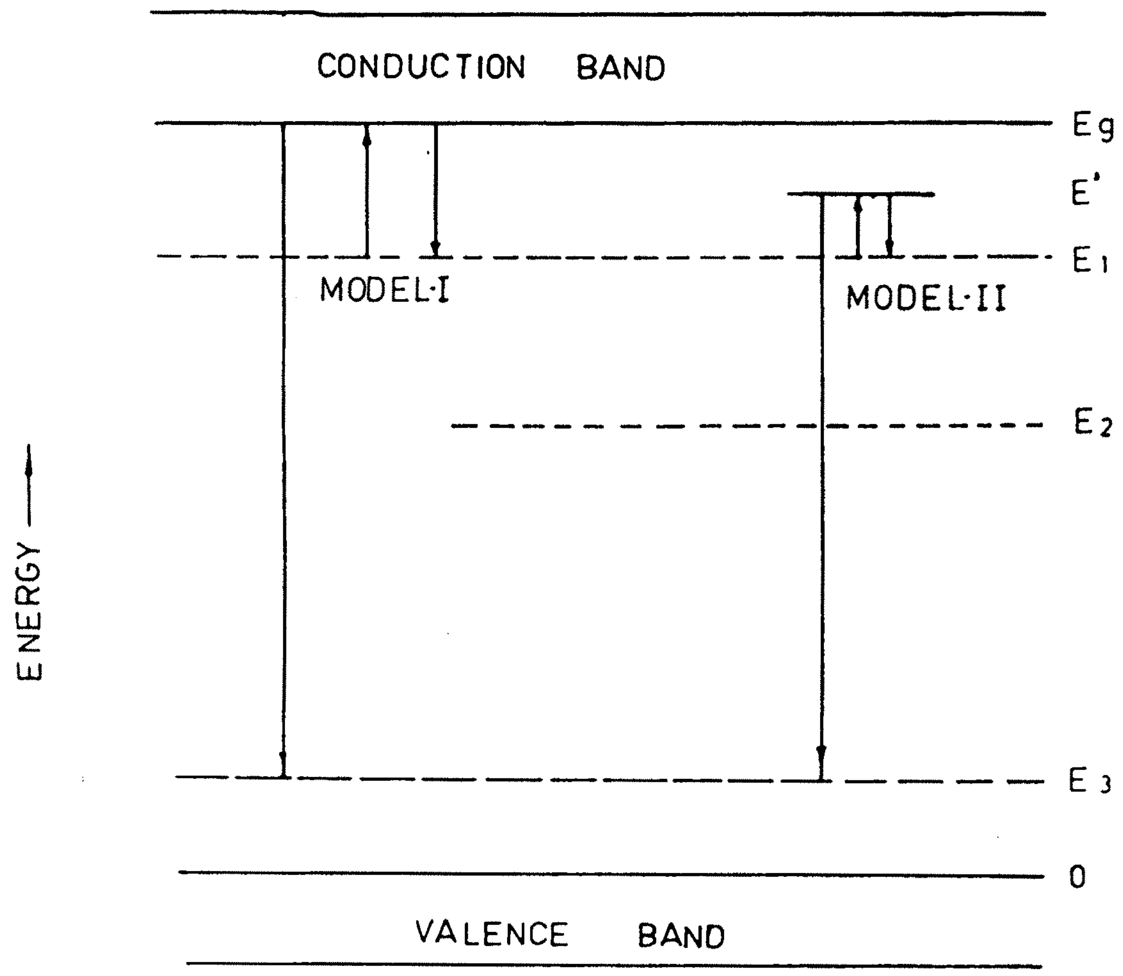
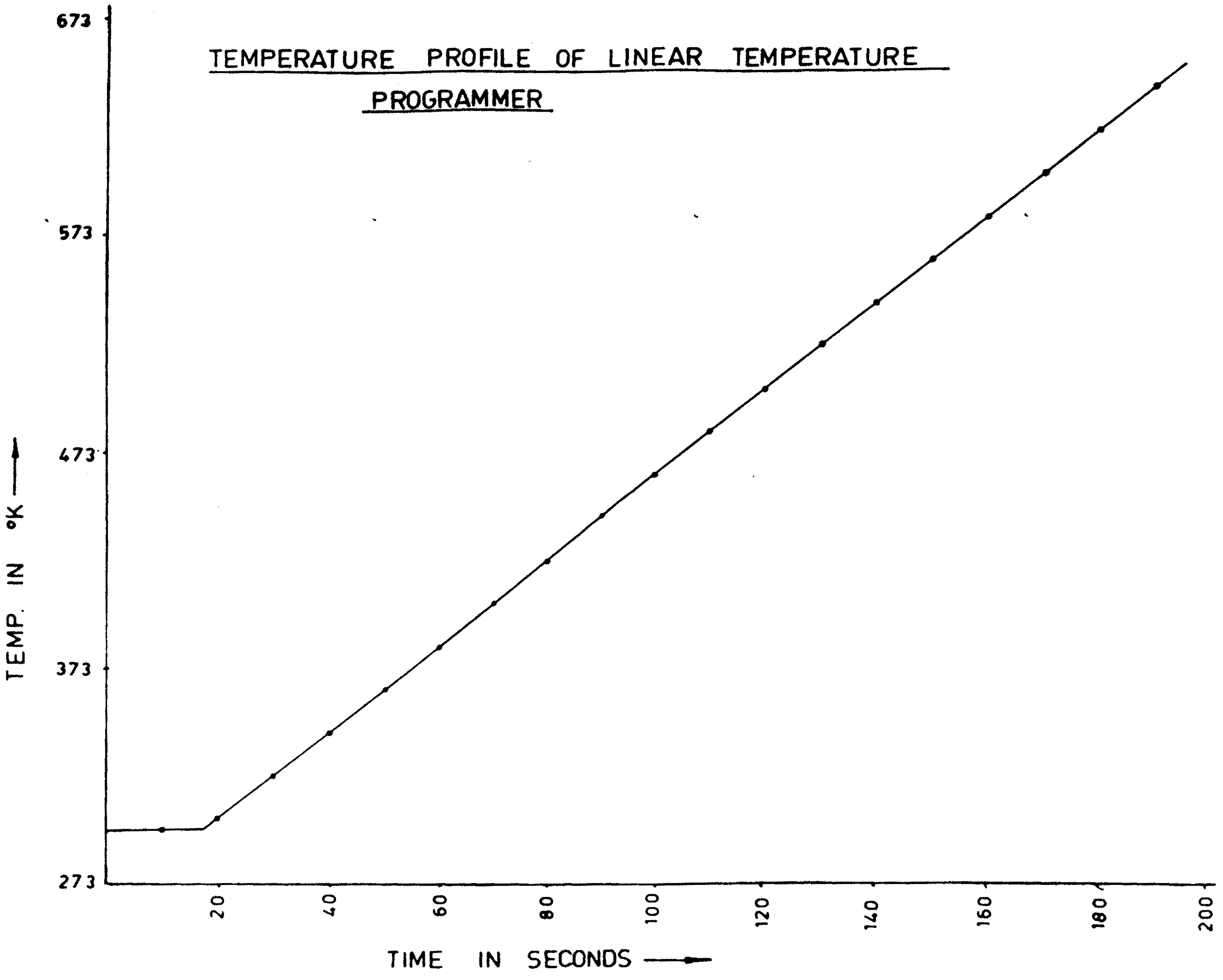


FIG. 4·1



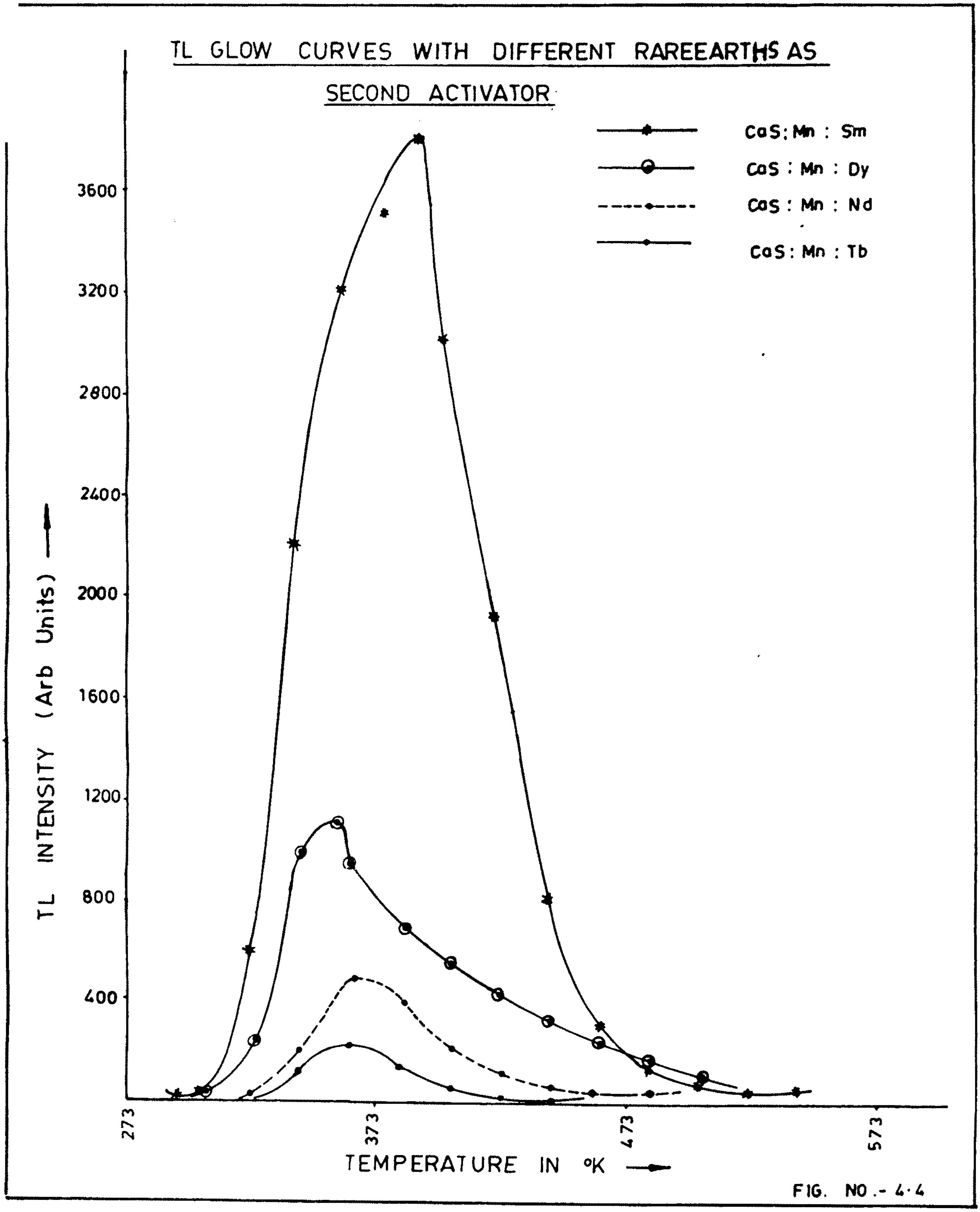
ENERGY BAND MODEL OF THERMOLUMINESCENCE

FIG. NO. - 4.2



TEMPERATURE PROFILE OF LINEAR TEMPERATURE PROGRAMMER

FIG. NO.- 4·3



TL GLOW CURVES WITH DIFFERENT RAREEARTHS AS SECOND ACTIVATOR

FIG. NO.- 4·4

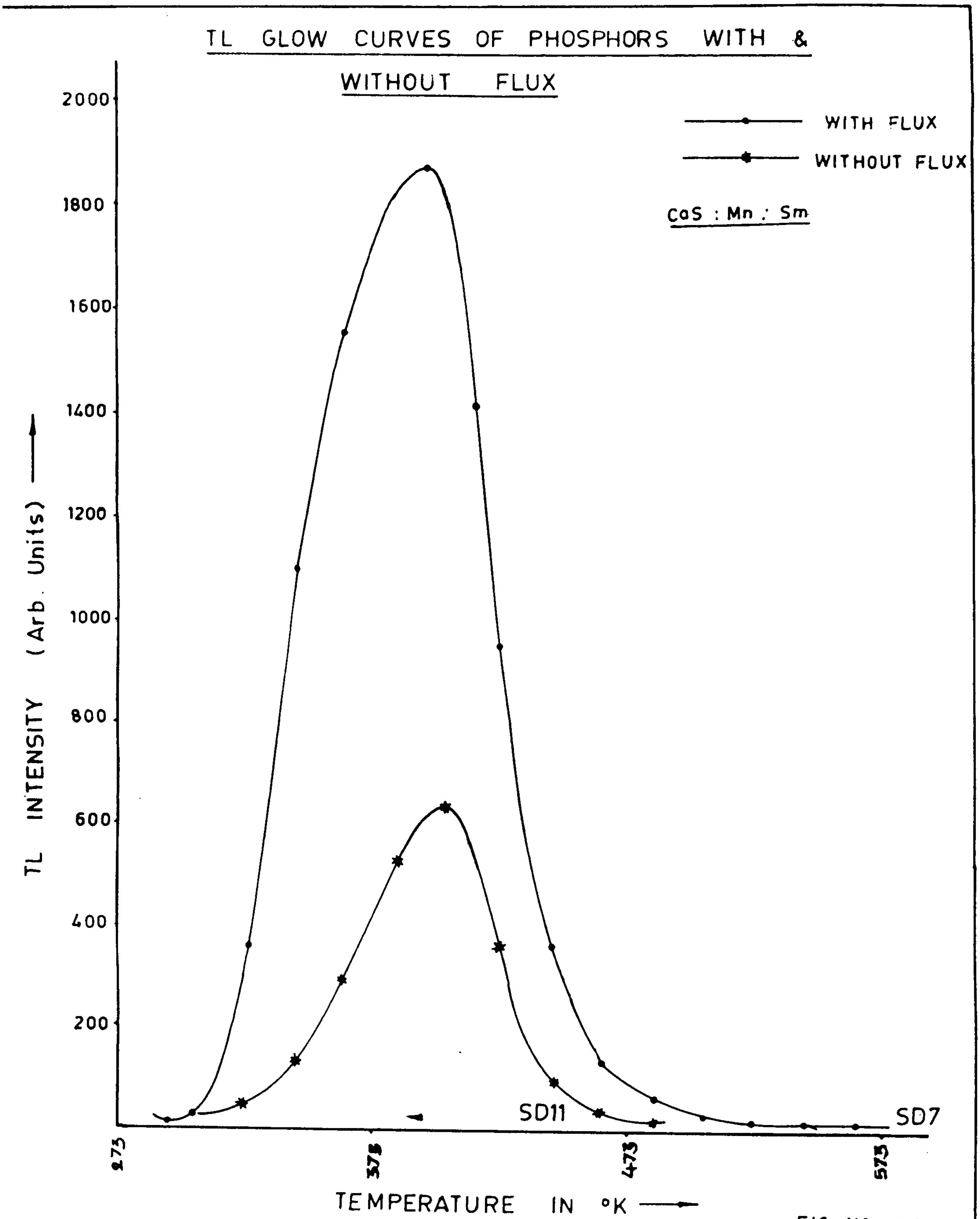

TL GLOW CURVES OF PHOSPHORS WITH & WITHOUT FLUX
WITH FLUX
WITHOUT FLUX
CaS : Mn : Sm
TL INTENSITY (Arb. Units)
2000
1800
1600
1400
1200
1000
800
600
400
200
SD11
SD7
273
373
473
573
TEMPERATURE IN °K

FIG. NO - 4.5

TL GLOW CURVES OF UNDOPED & DOPED PHOSPHORS

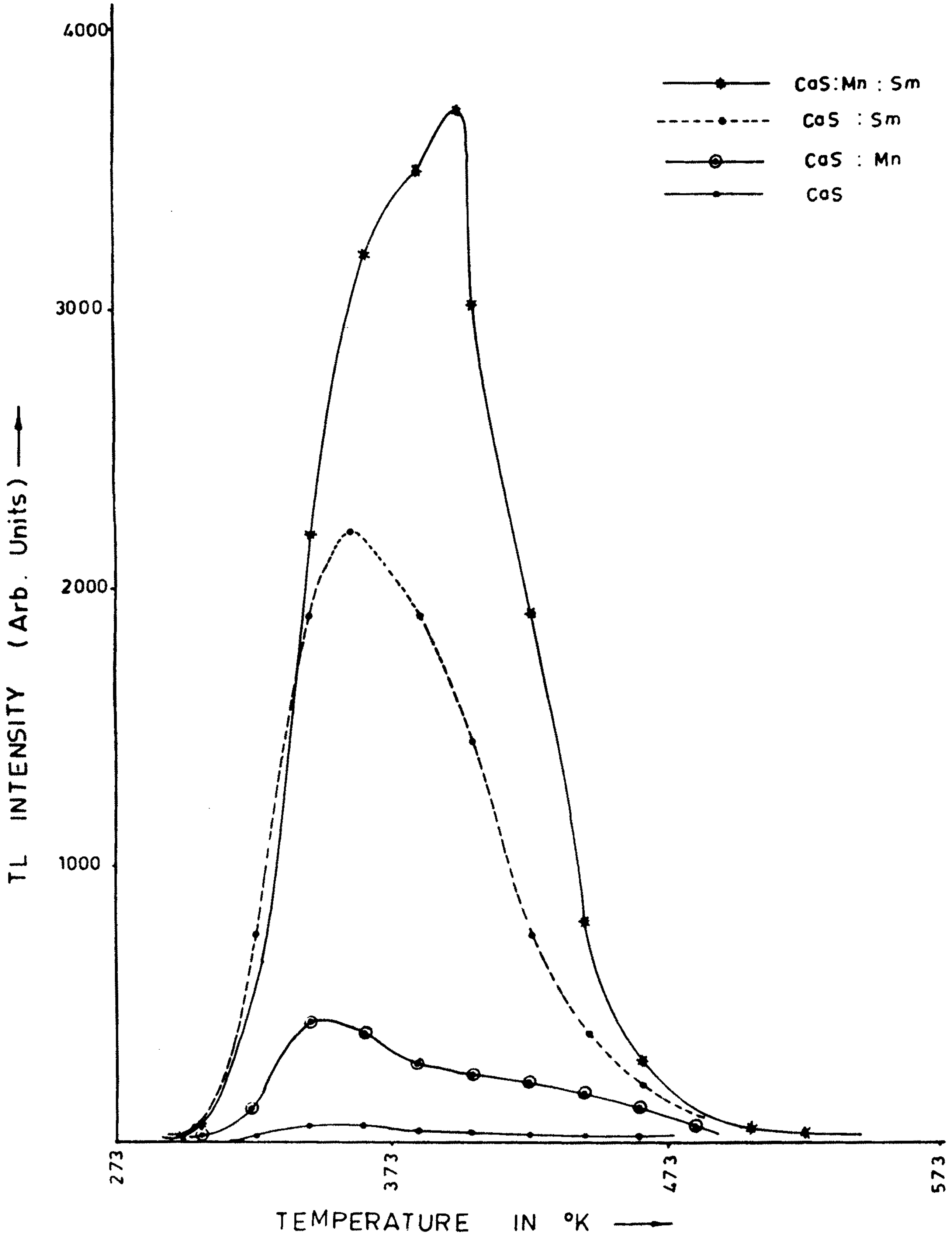


FIG. NO.-4·6

UV EXCITED SAMPLES

GLOW CURVES FOR CaS : Mn : Sm PHOSPHORS

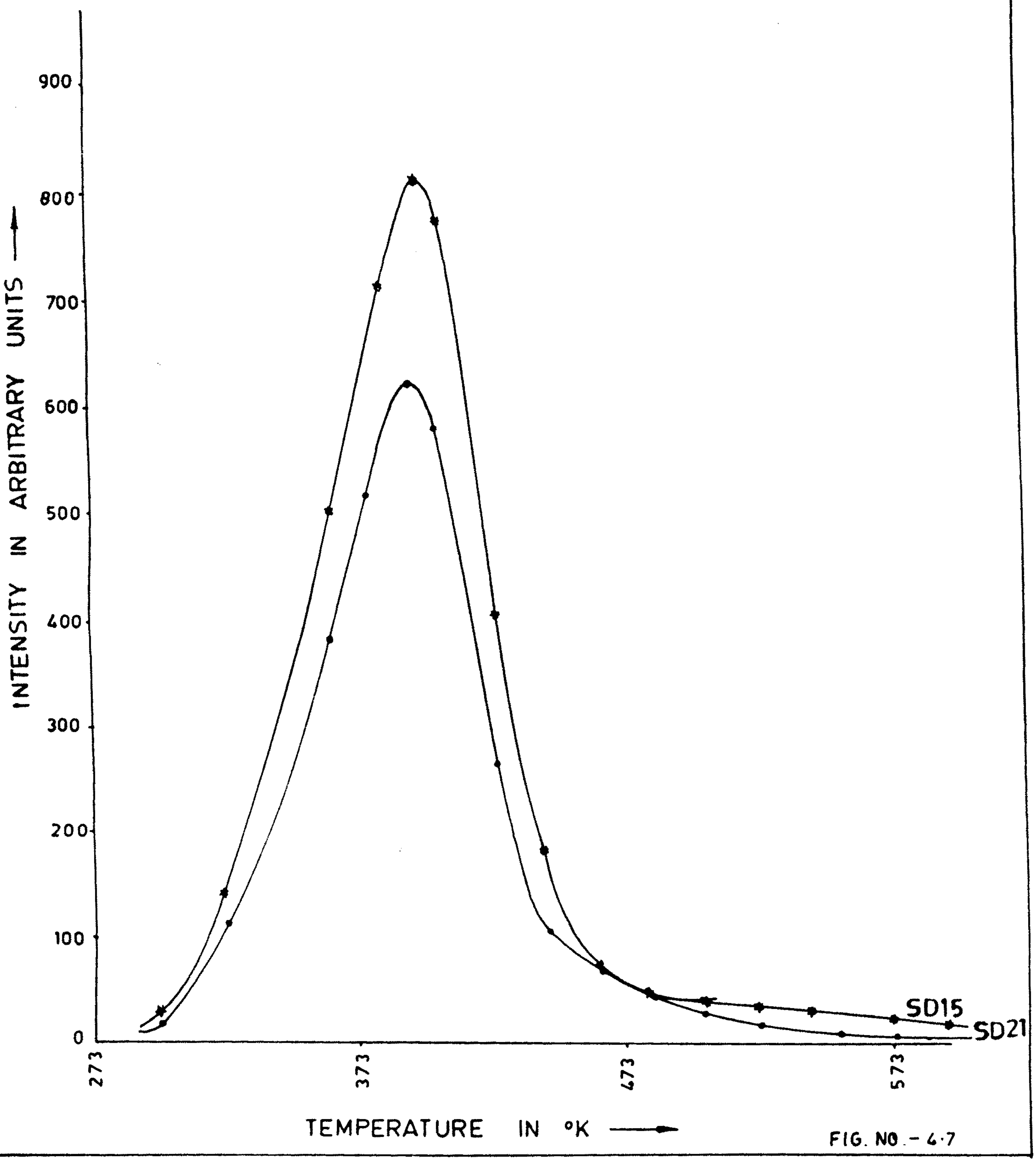


FIG. NO. - 4·7

UV EXCITED SAMPLES

GLOW CURVES FOR CaS : Mn : Sm PHOSPHORS

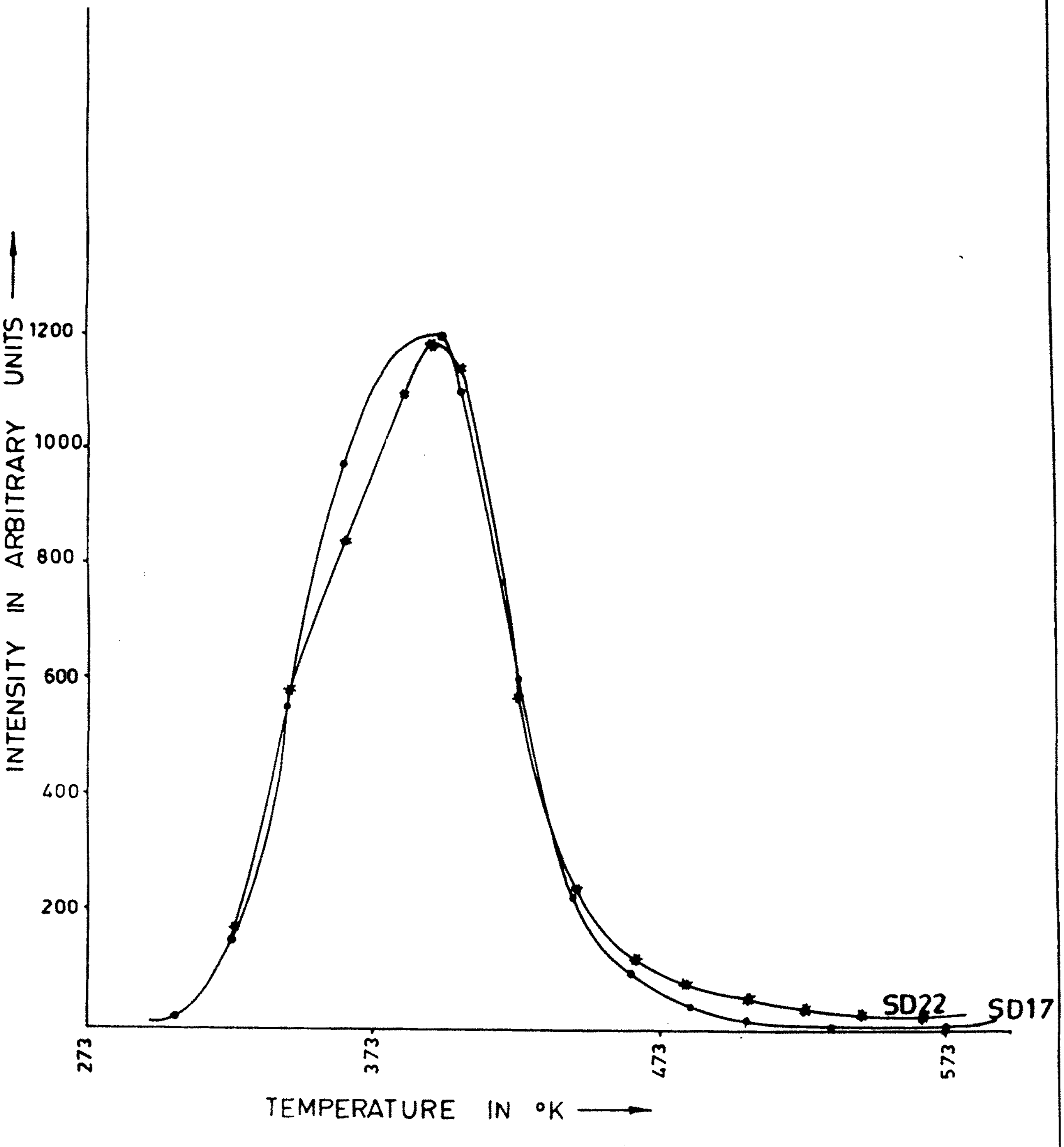


FIG. NO. - 4.8

UV EXCITED SAMPLES

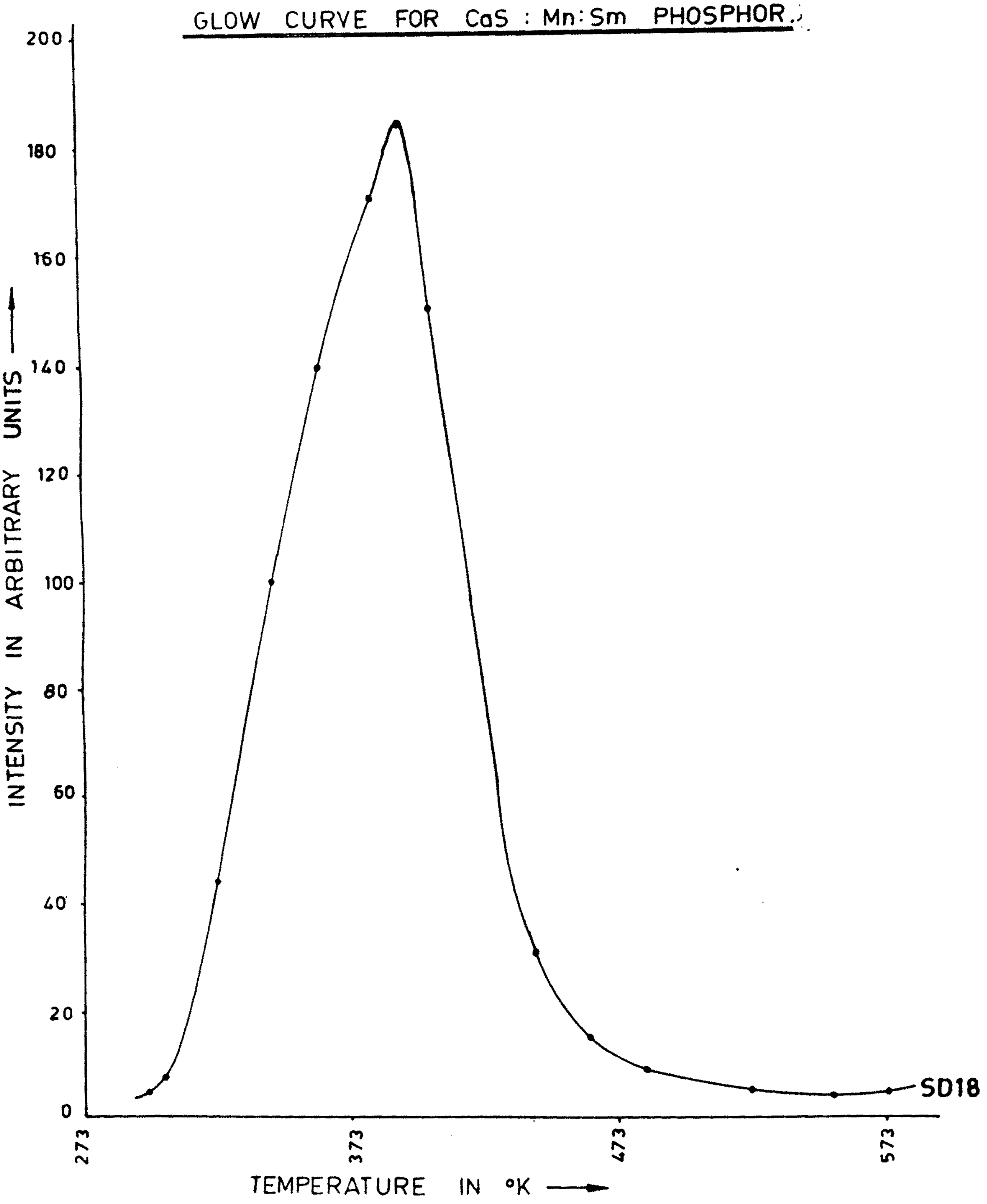


FIG. NO.- 4·9

UV EXCITED SAMPLES

GLOW CURVE FOR CaS : Mn : Sm PHOSPHOR

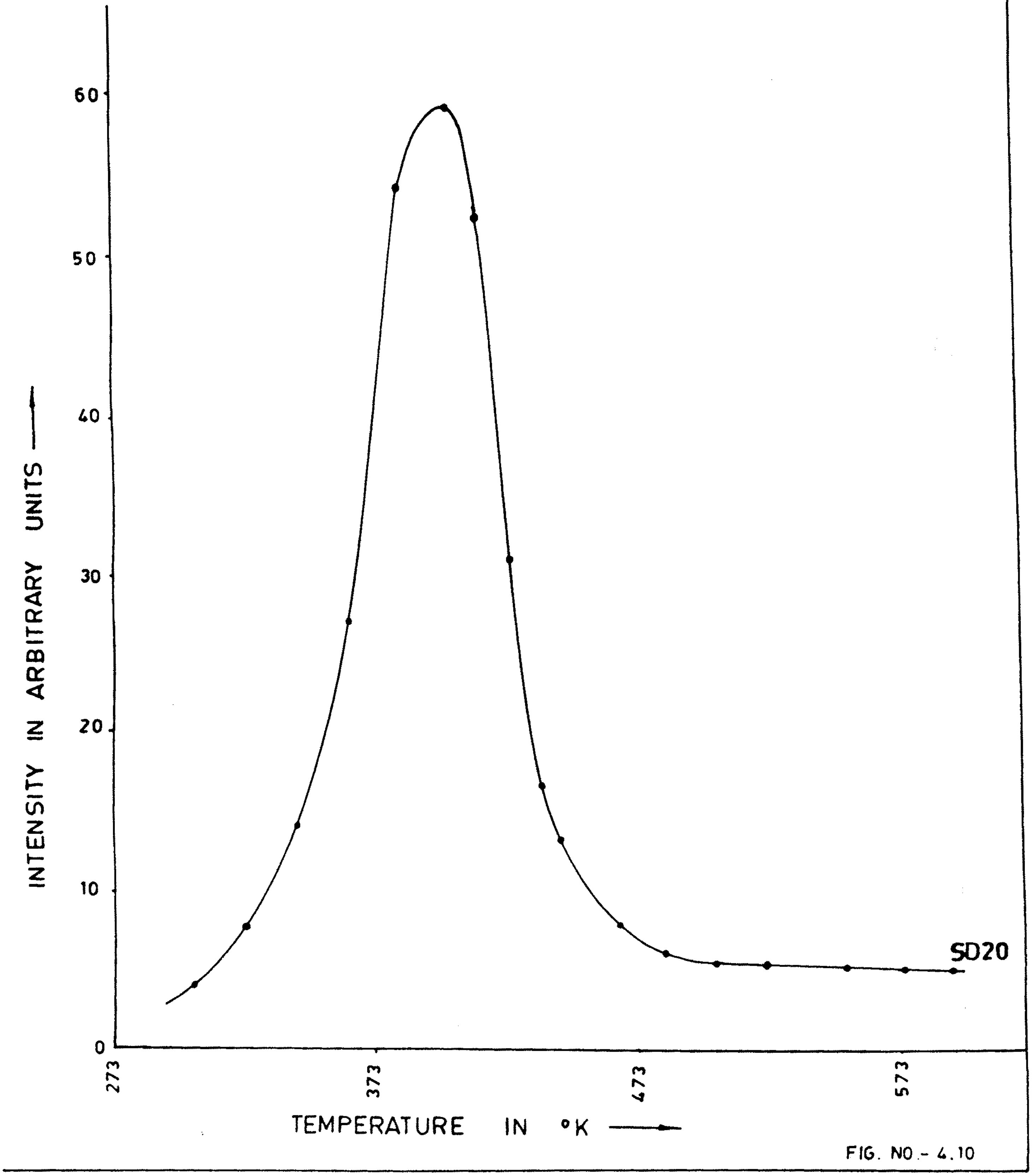


FIG. NO.- 4.10

UV EXCITED SAMPLES

GLOW CURVES FOR CaS : Mn : Sm PHOSPHORS

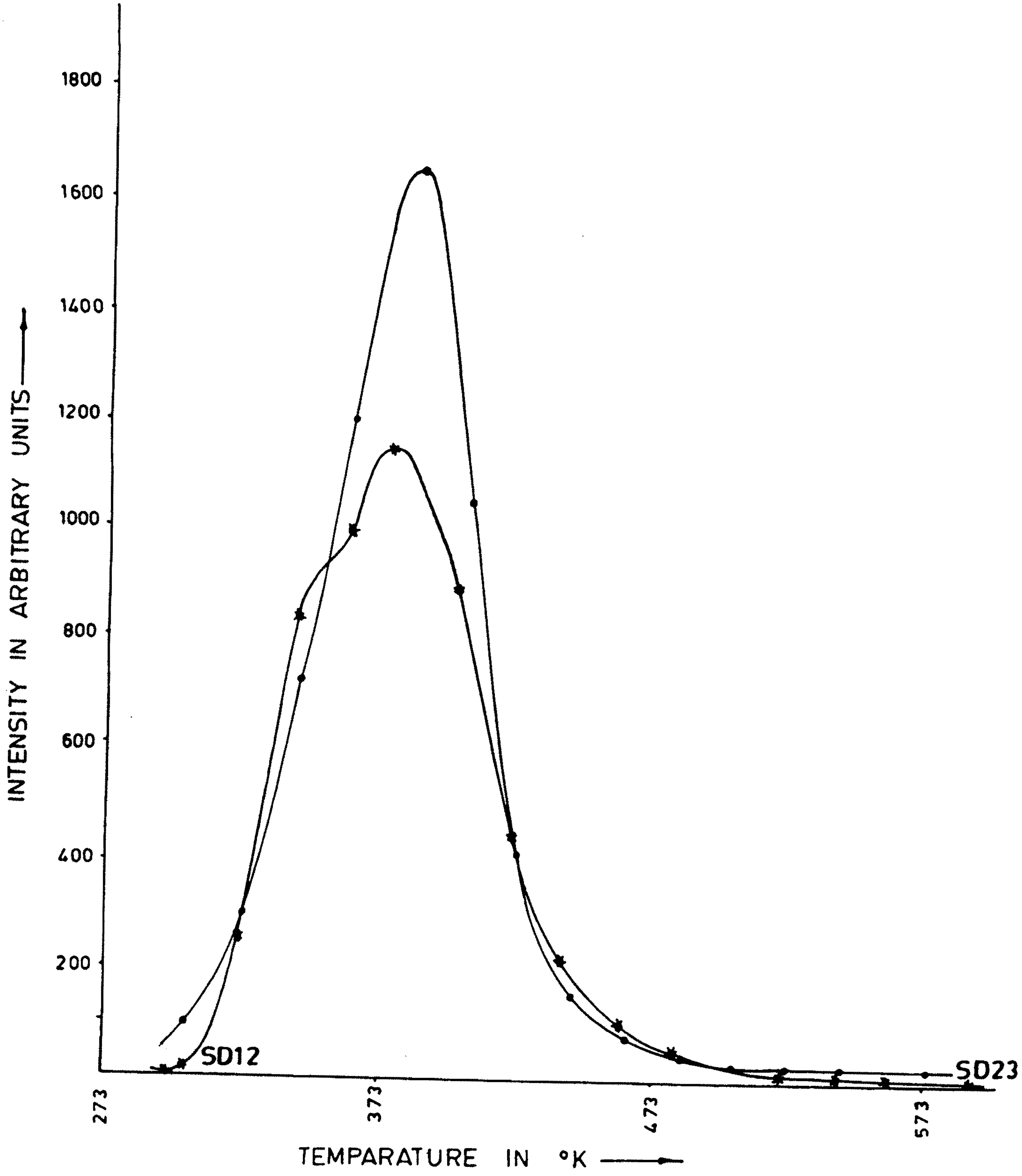


FIG. NO.- 4.11

UV EXCITED SAMPLES

GLOW CURVE FOR CaS : Mn : Sm PHOSPHOR

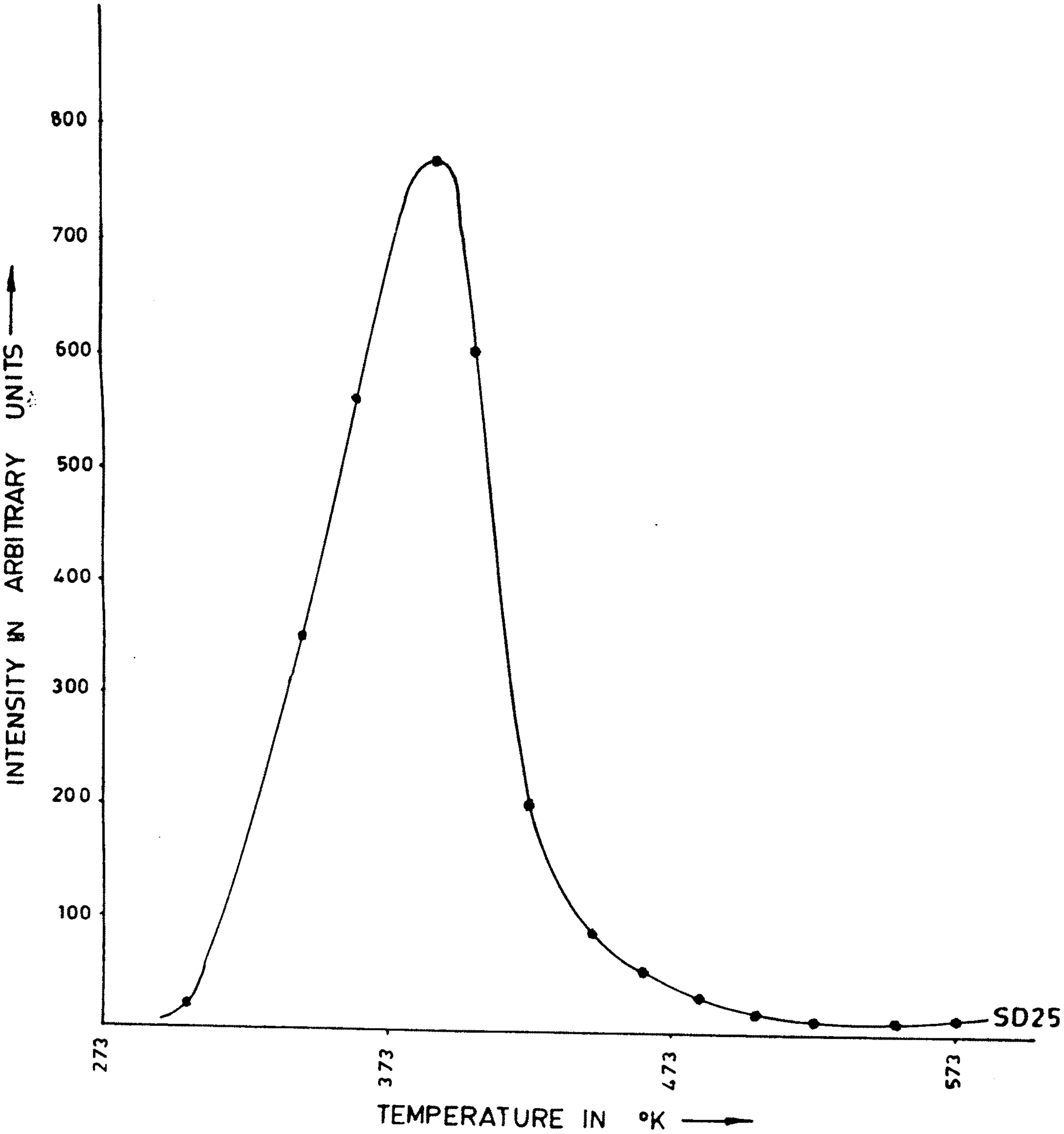


FIG. NO.- 4·12

UV EXCITED SAMPLES

GLOW CURVES FOR CaS : Mn : Sm PHOSPHORS

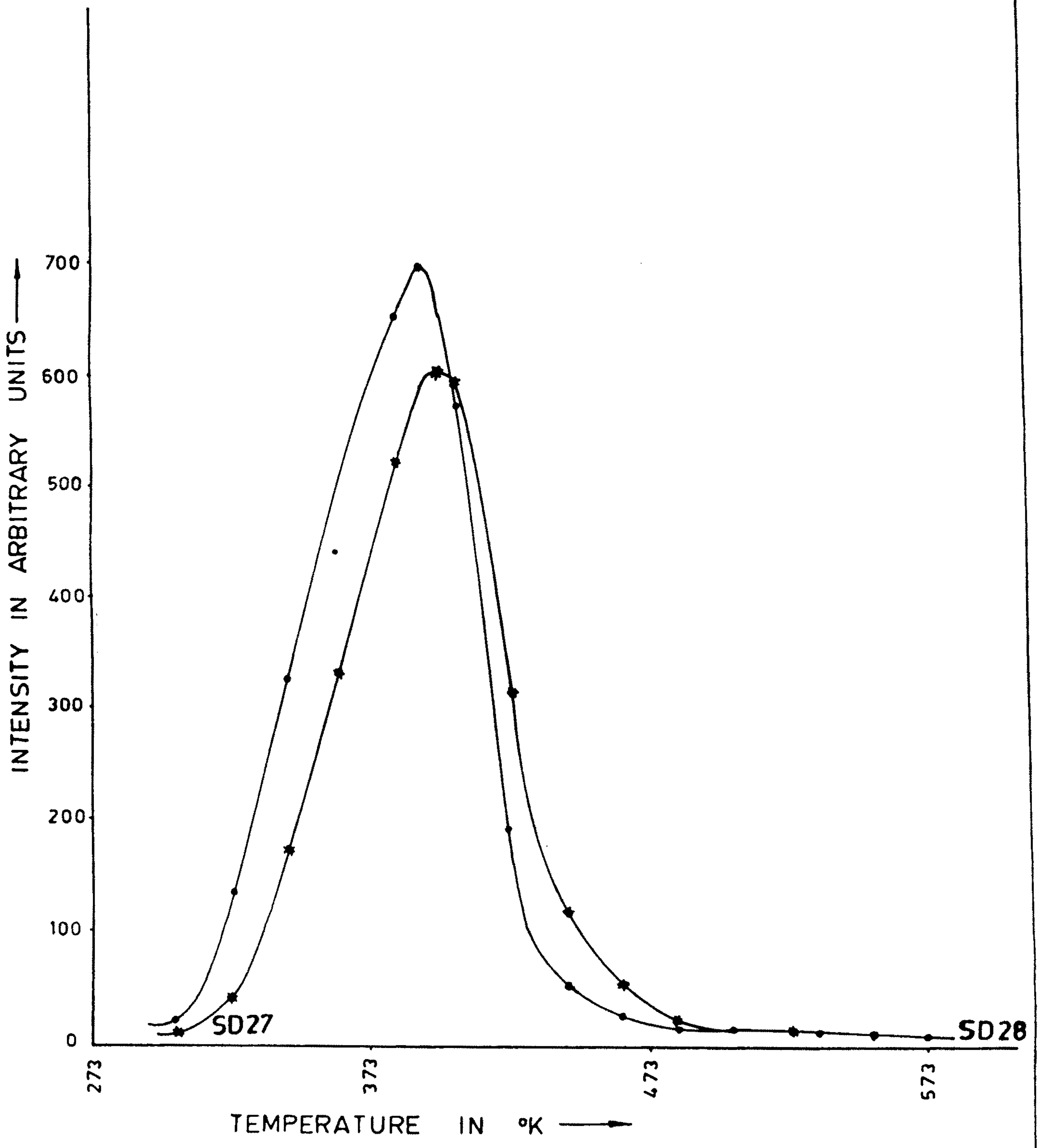
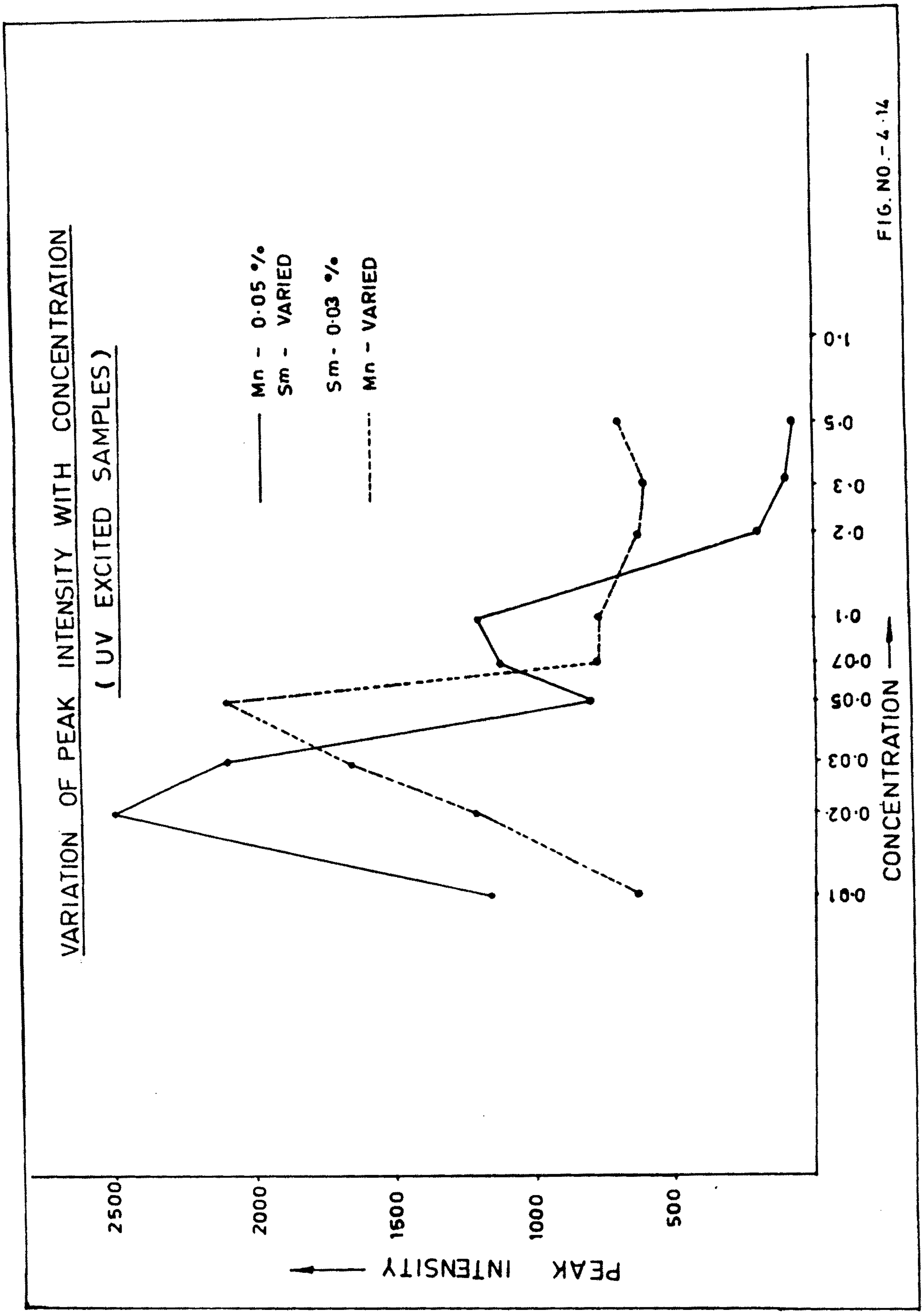


FIG. NO.— 4·13



VARIATION OF PEAK INTENSITY WITH CONCENTRATION
(UV EXCITED SAMPLES)

FIG. NO. - 4.14

ARRHENIUS PLOTS

(INITIAL RISE METHOD)

SD14 · UV EXCITATION

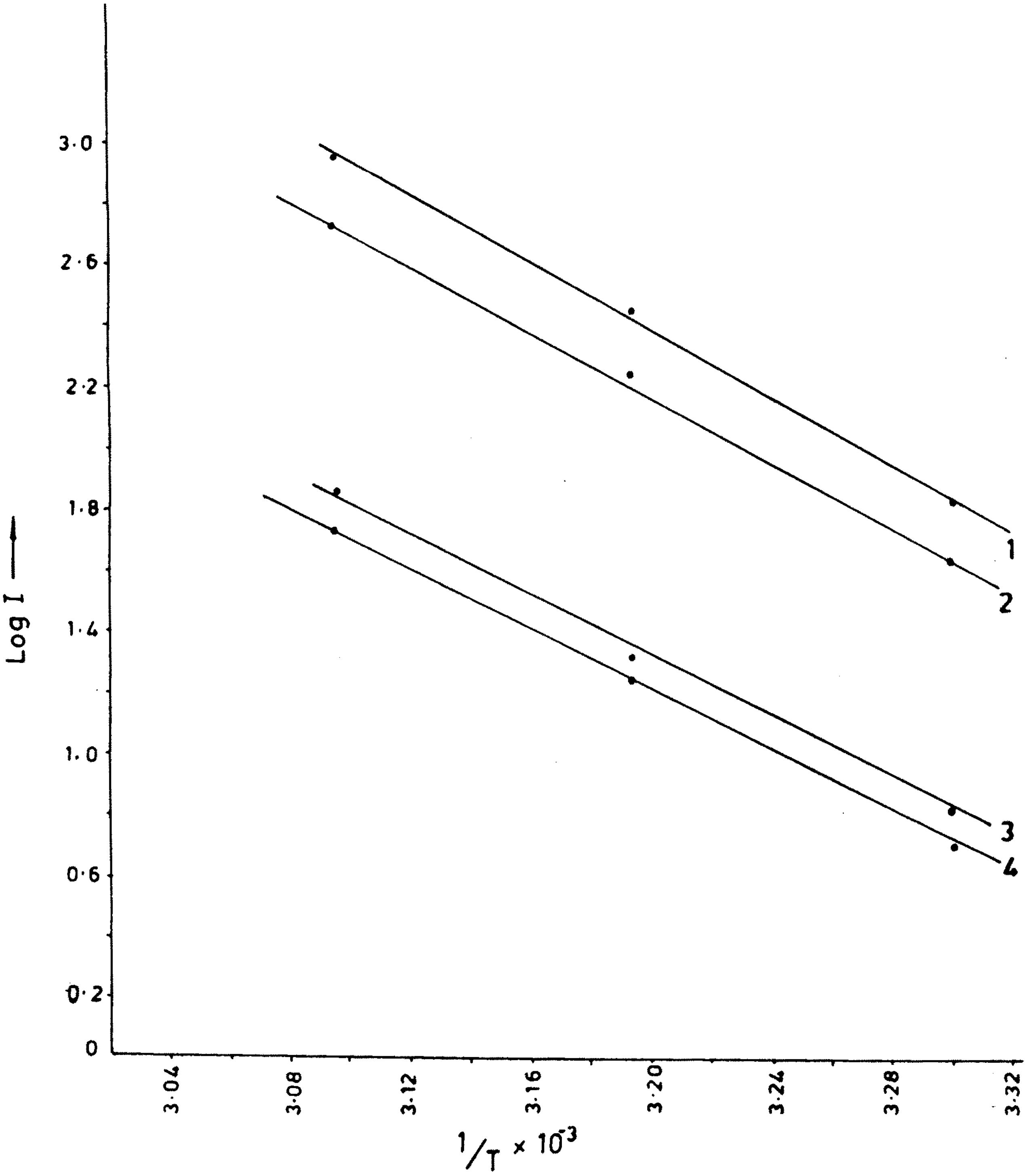


FIG. NO.- 4·15

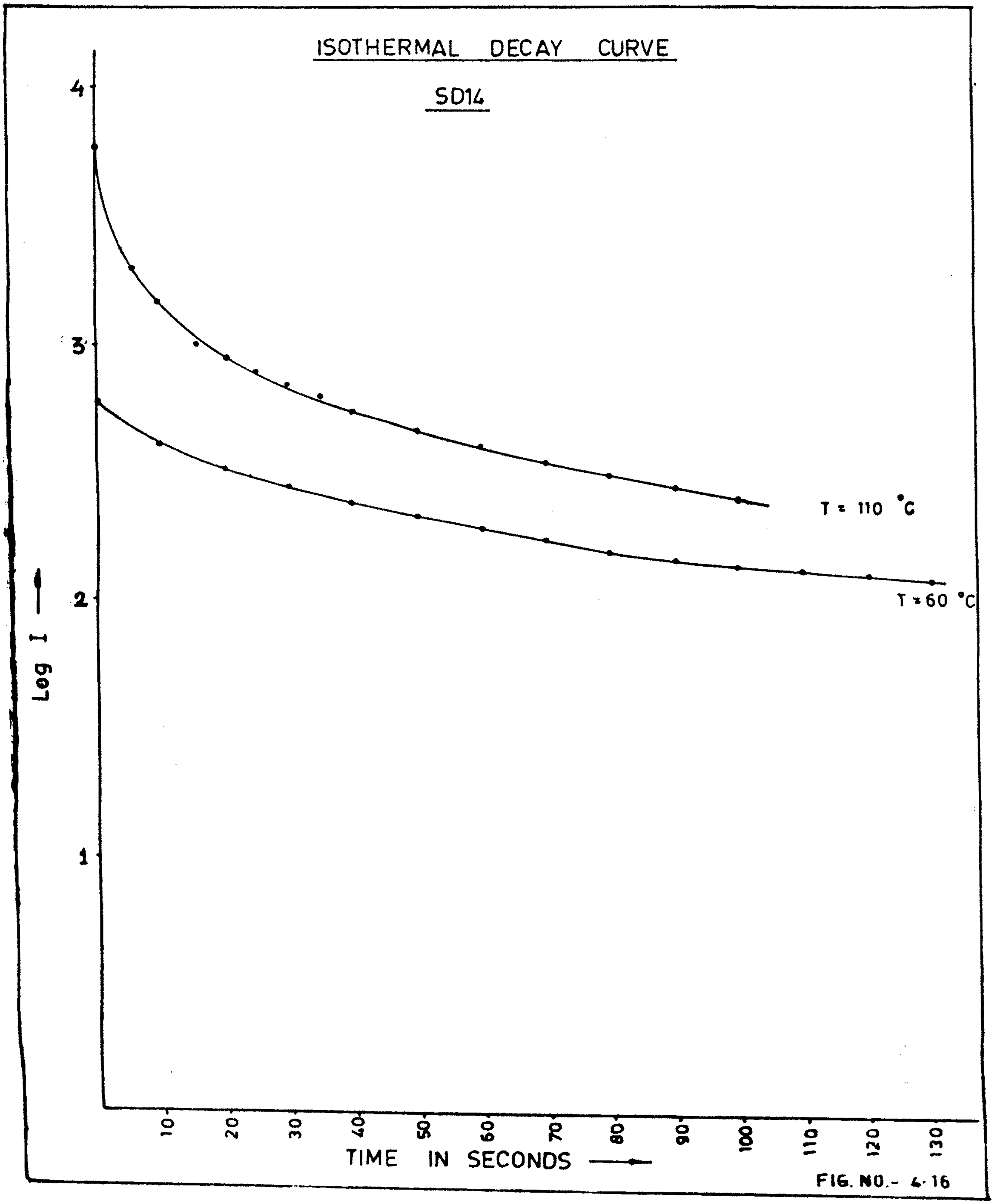

ISOTHERMAL DECAY CURVE
SD14
Log I
4
3
2
1
T = 110 °C
T = 60 °C
10
20
30
40
50
60
70
80
90
100
110
120
130
TIME IN SECONDS

FIG. NO.- 4·16

PLOTS OF $1/\sqrt{I}$ Vs TIME
(ISOTHERMAL DECAY METHOD)

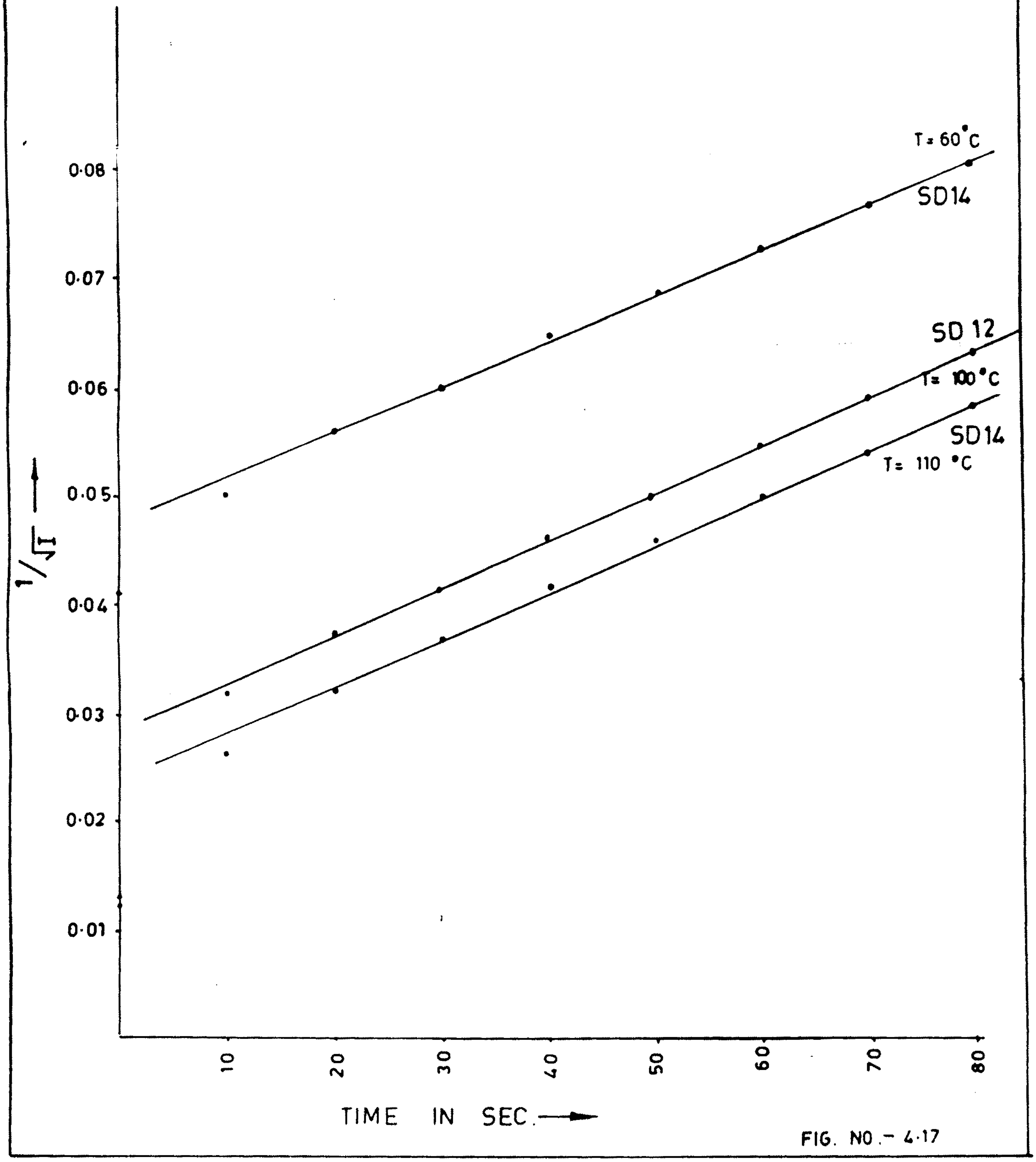


FIG. NO.- 4·17

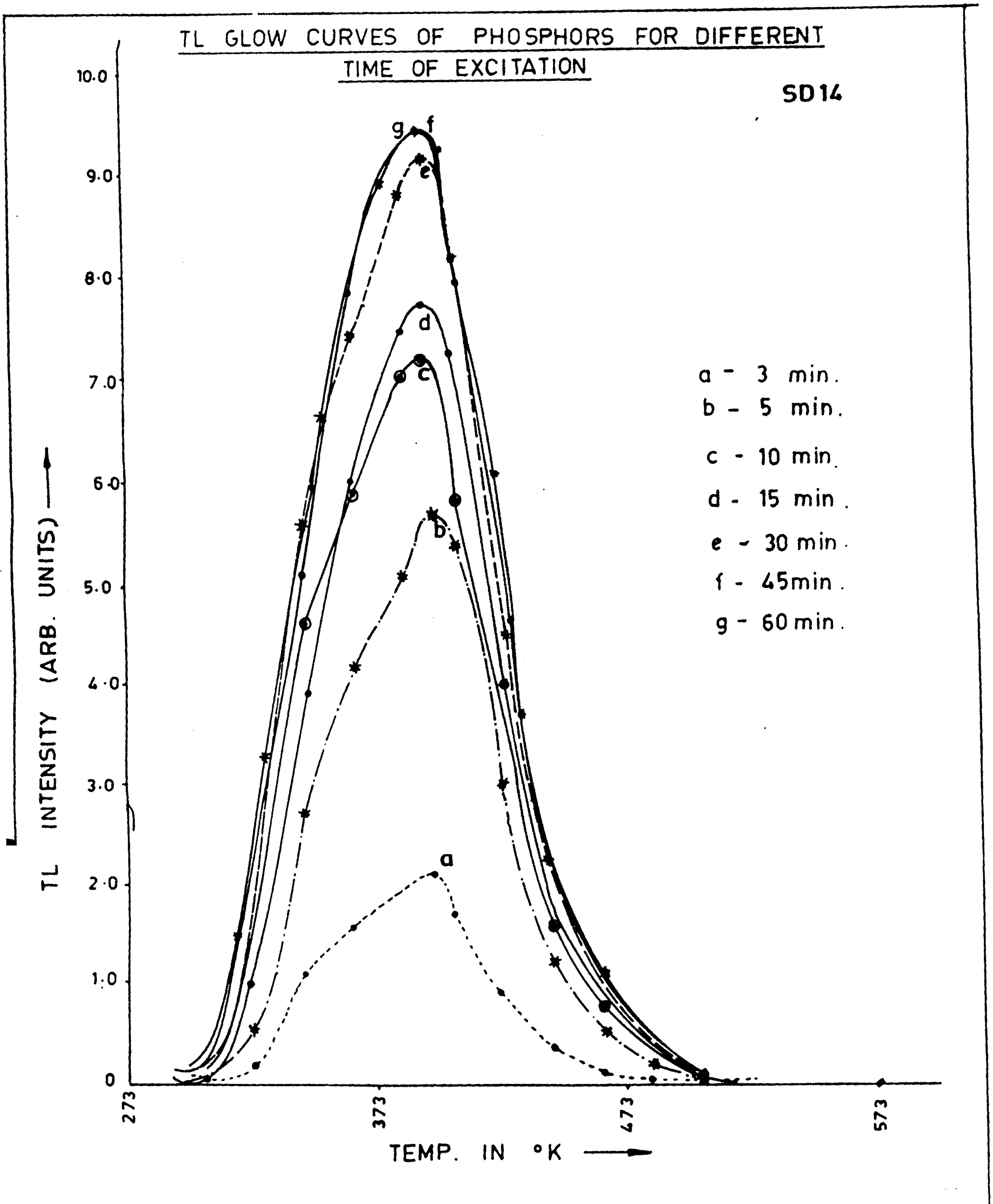

TL GLOW CURVES OF PHOSPHORS FOR DIFFERENT TIME OF EXCITATION
SD14
TL INTENSITY (ARB. UNITS)
10.0
9.0
8.0
7.0
6.0
5.0
4.0
3.0
2.0
1.0
0
273
373
473
573
TEMP. IN °K
g
f
e
d
c
b
a
a - 3 min.
b - 5 min.
c - 10 min.
d - 15 min.
e - 30 min.
f - 45min.
g - 60 min.

FIG. NO – 4.18

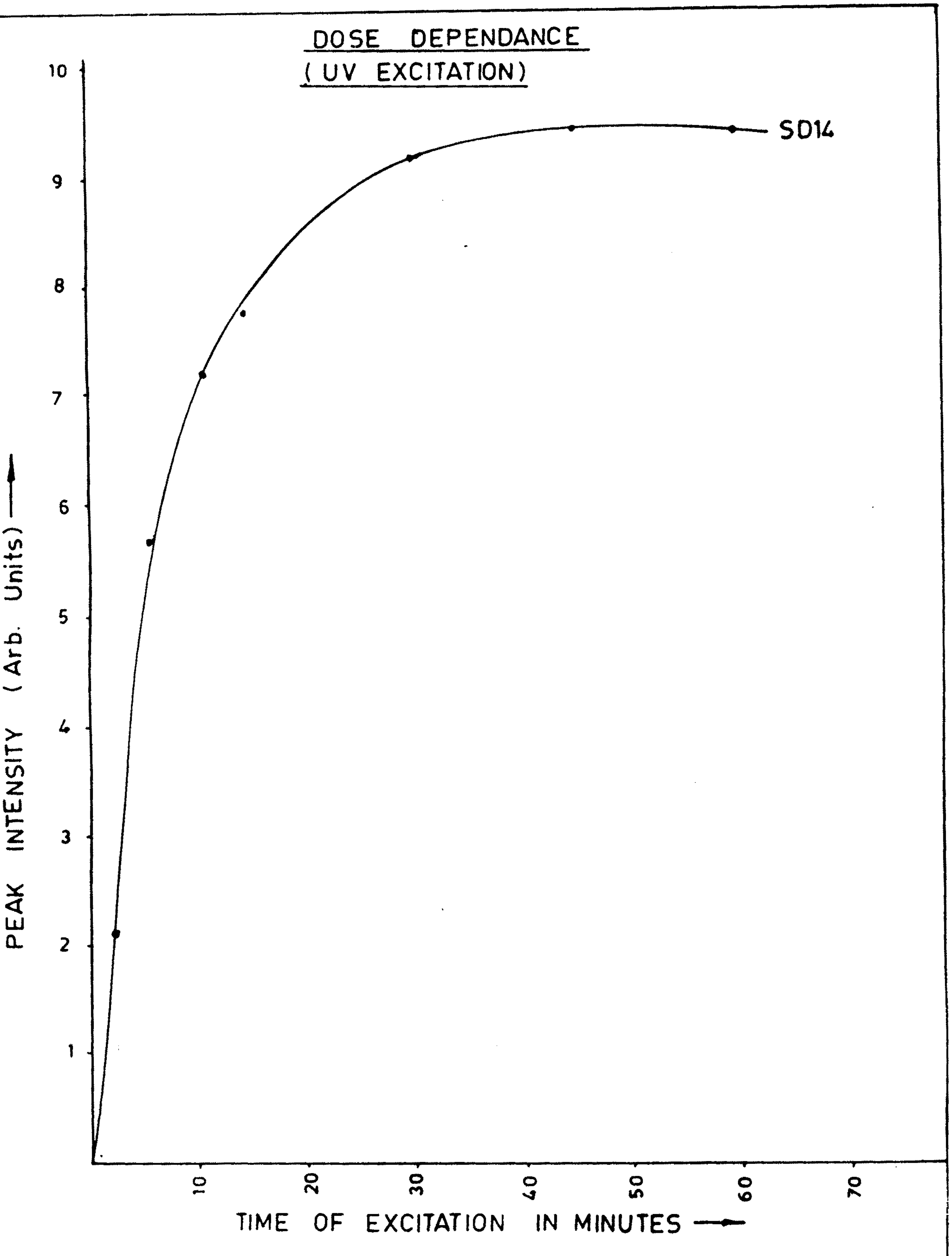

DOSE DEPENDANCE
(UV EXCITATION)
SD14
PEAK INTENSITY (Arb. Units)
TIME OF EXCITATION IN MINUTES
1
2
3
4
5
6
7
8
9
10
10
20
30
40
50
60
70

FIG. NO. - 4·19

γ IRRADIATED SAMPLES

GLOW CURVE FOR CaS : Mn : Sm PHOSPHORS

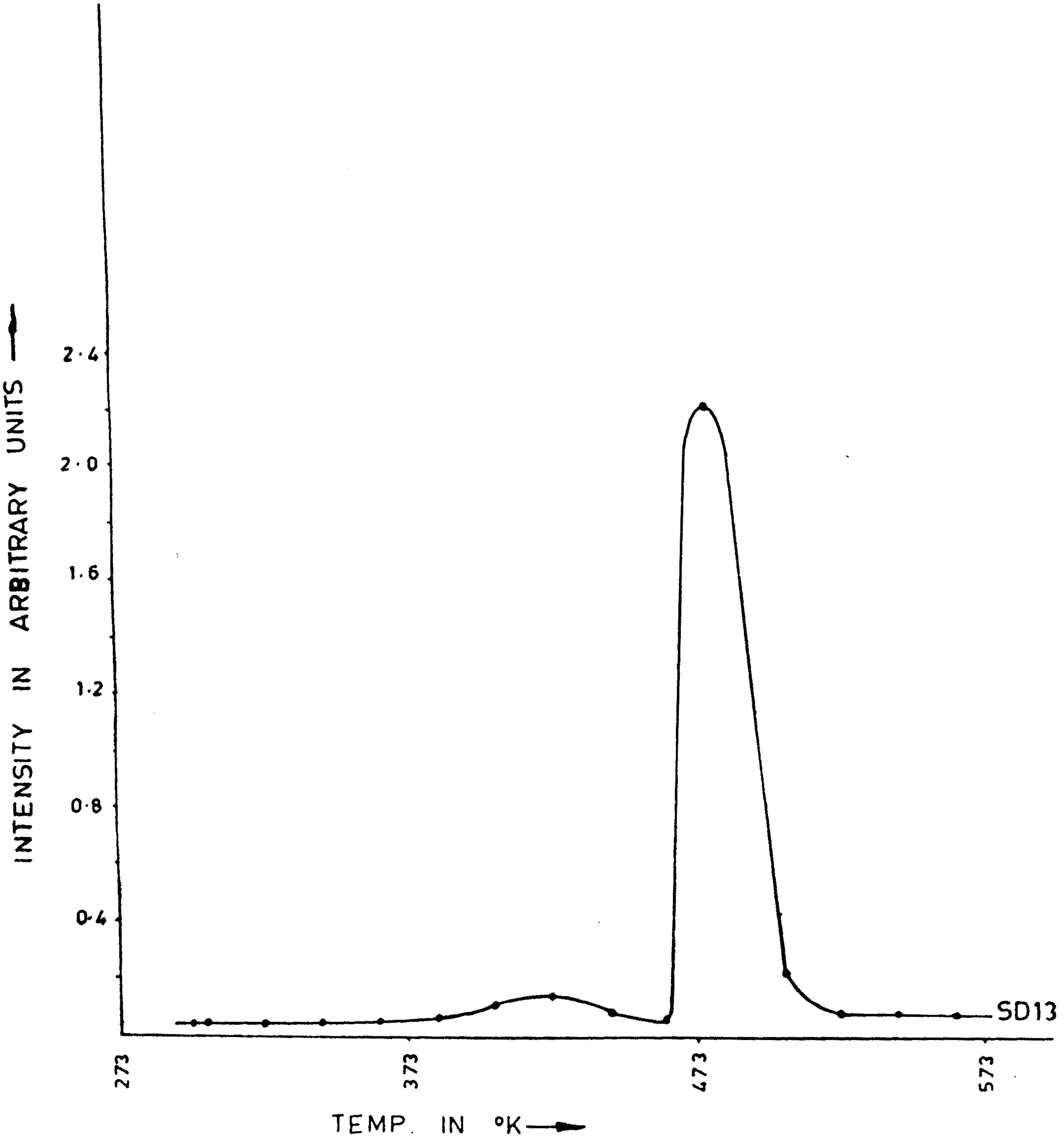


FIG. NO.-4·20

γ IRRADIATED SAMPLES

GLOW CURVE FOR CaS : Mn : Sm PHOSPHORS

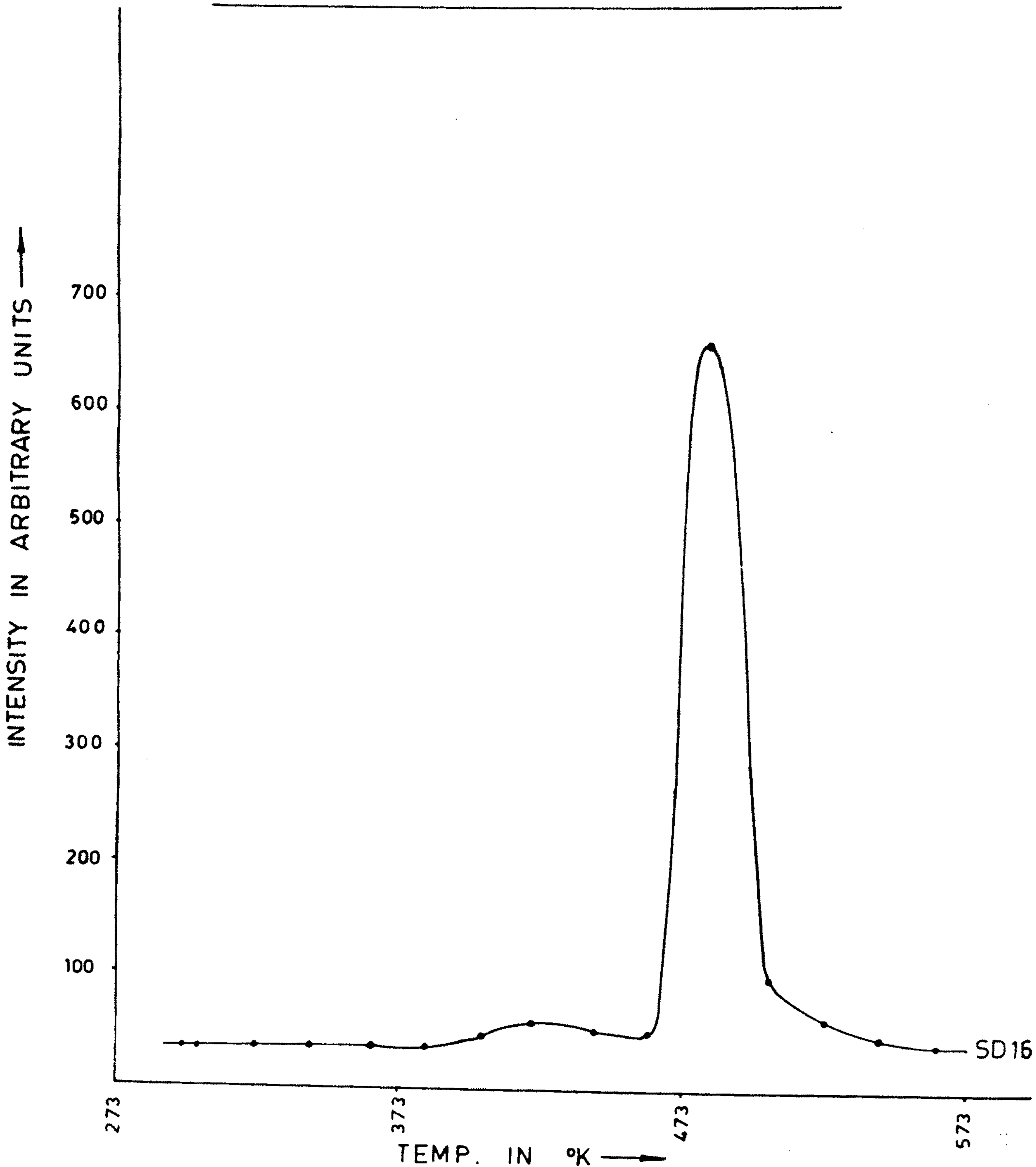


FIG. NO - 4·21

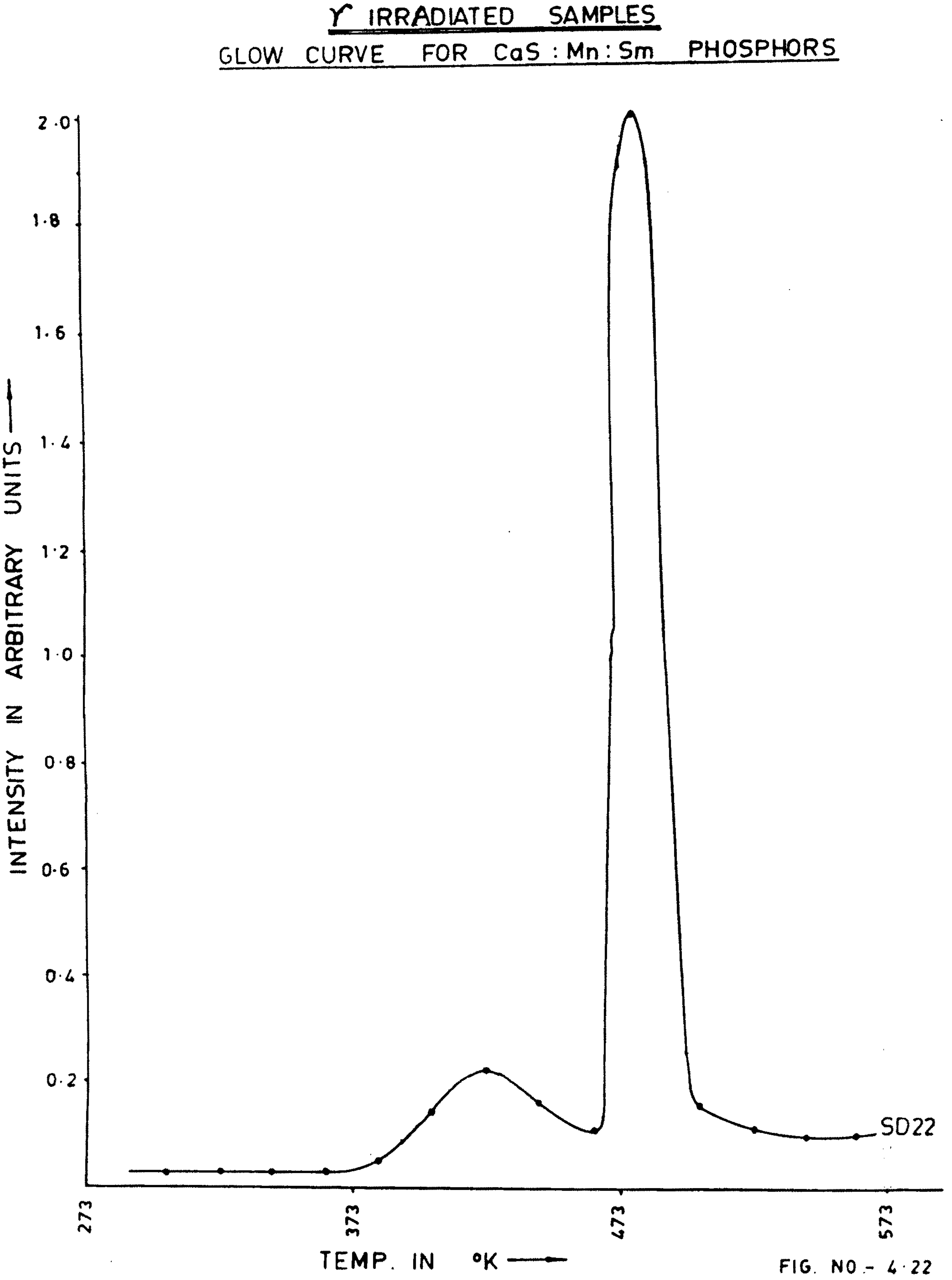

γ IRRADIATED SAMPLES
GLOW CURVE FOR CaS : Mn : Sm PHOSPHORS
2·0
1·8
1·6
1·4
1·2
1·0
0·8
0·6
0·4
0·2
INTENSITY IN ARBITRARY UNITS
273
373
473
573
TEMP. IN °K
SD22

FIG. NO - 4·22

γ IRRADIATED SAMPLES

GLOW CURVE FOR CaS : Mn : Sm PHOSPHORS

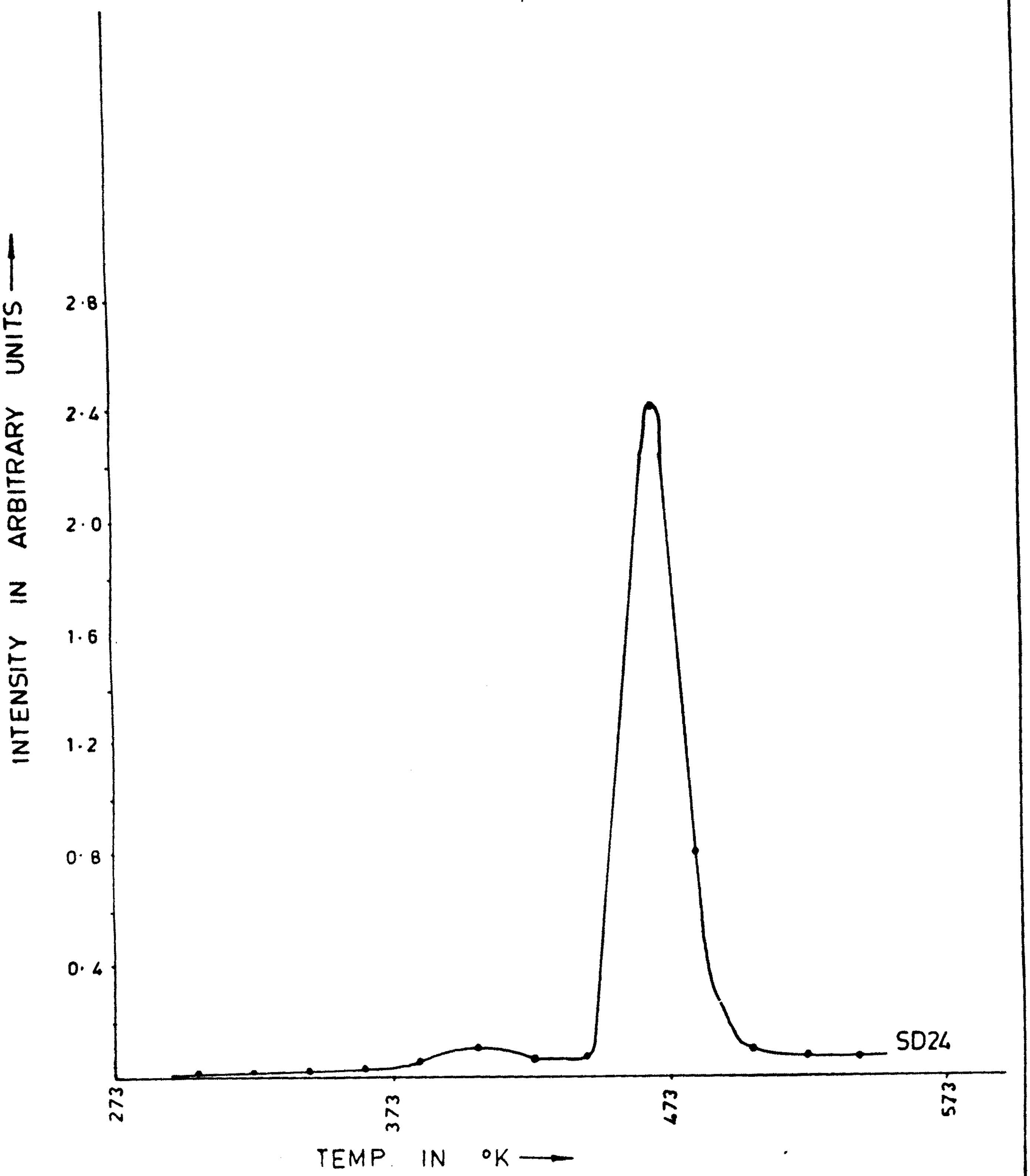


FIG. NO.- 4·23

γ IRRADIATED SAMPLES

GLOW CURVE FOR Ca : Mn : Sm PHOSPHORS

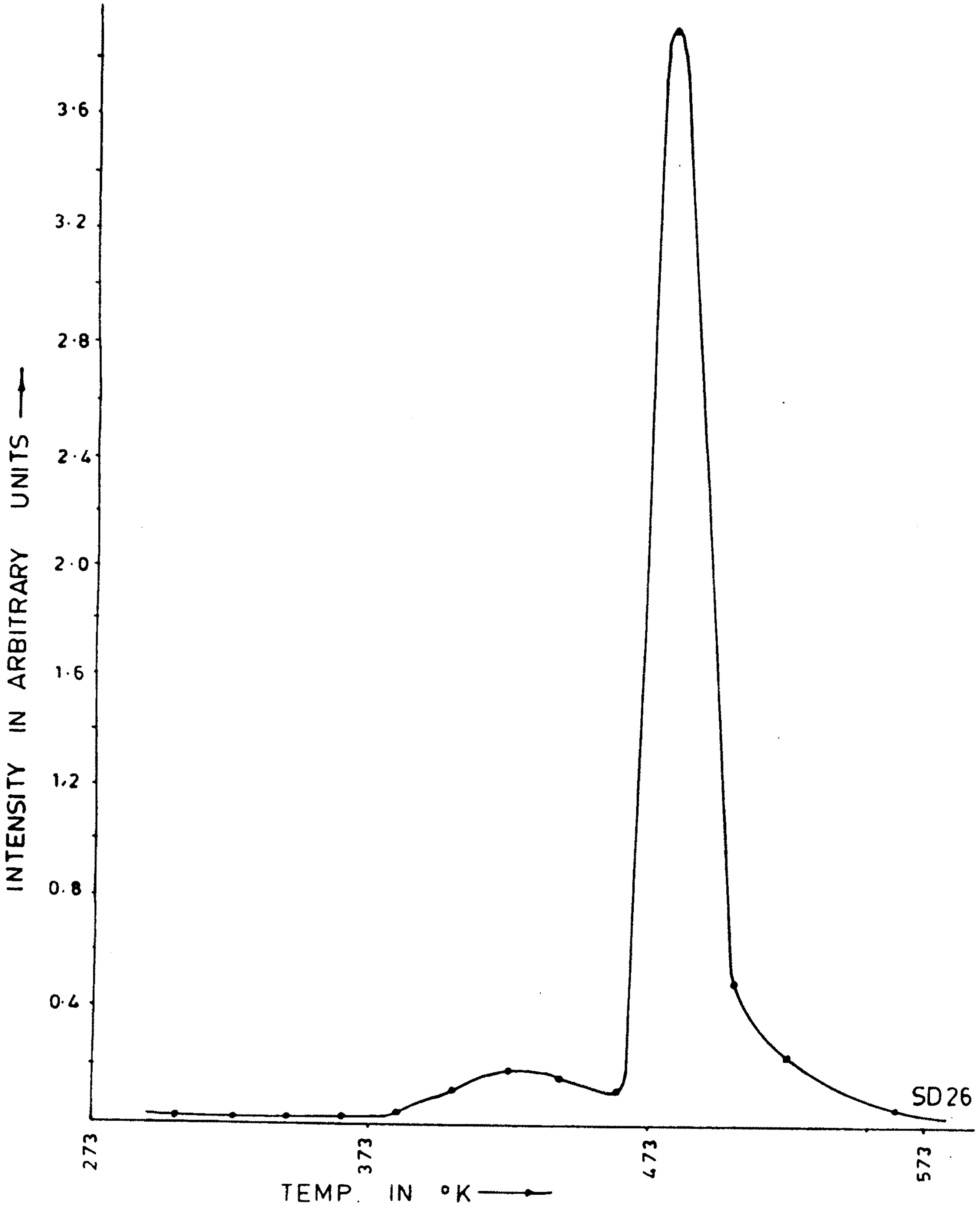


FIG. NO - 4·24