CHAPTER IV

THERMOLUMINESCIENCE

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4.1 : INTRODUCTION :

Thermoluminescence is a phenomenon mostly created in artificially prepared phosphors. This property depends on nature of host material , nature of impurity in the host material , the process / condition of doping the impurity and irradiation source on the phosphors.

.TL study can be done with the help of TL glow curve. (Which includes rate of heating the sample). From the glow curve, amount of energy stored by imperfect crystals can be determined which is known as trap depth or activation energy (E) frequency factor (S), and nature of kinetics. The theoretical aspects and their details are included in this chapter.

The object of the present investigation is to analyse the observed glow curves for the samples containing varying percentage of Sm : Nd and Dy : Tb and to determine activation energy and the escape frequency factor. The nature and origin of traps responsible in TL process and their size have been investigated An attempt has been made to determine the type of kinetics involved in thermoluminescence process.

4.2 : THEORETICAL ASPECTS :

4.2.1 : Theory of thermoluminescence :

By studing glow curve Randall and Wilkins (1) gave theoretical aspect. According to them, the impurity and lattice defect which give rise to localised energy levels in the forbidden region constitute the electron traps, hole traps and metastable state. The electrons in metastable states are raised thermally to an excited state from which they return to the ground state with emission of radiation. Randall & Wilkins assumed this to be monomoleculer kinetics or first order kinetics and come to a conclusion that the decay of such phosphors is exponontial. For this case they neglected the retrapping of electrons in the empty traps

Garlick and Gibson (2) have put forth a theory developed by taking in account of equal probabilities for the retrapping and recombination of released electron which is known as bimolecular kinetics or second order kinetics (a straight line graph obtained by plotting $(I)^{-\frac{1}{2}}$ against time). Electrons in the traps have a Maxwellian distribution of thermal energies (1). Therefore, the probability (P) of escape of electron persecond from a trap of depth E (actication energy) is of the form (Arrhenious factor)

$$P = S \; e^{-E/KT}$$

Where K is Boltzmann constant and T is temperature in °K . S has a unit $(\text{Sec})^{-1}$ and is hence called the frequency factor. The factor S is a constant but some times it is found to be dependent on the initial concentration of trapped electrons (3) in a given type of traps.

4.2.2 : First order kinetics : Randall and Wilkins Theory :

Randall and Wilkins (1) provided a simple theory for TL glow peak. They assumed that the electrons released on heating are not retrapped but all of these go to the recombination (luminescence) centres resulting in thermoluminescence. Therefore TL intensity proportional to the rate of release of electrons from the trap.

$$I \propto \frac{dn}{dt} = - cpn. \qquad \text{--- (4.2)}$$

$$= - cns \,/\, \exp.(- E/KT)$$

Where n is the number of trapped electrons and c is a constant, Rearranging,

$$\frac{dn}{n} = - cse^{- E/KT} \frac{dt}{dT} \, dT.$$

$$= - c \frac{s}{\beta} e^{- E/KT} .dT$$

Where $\beta = dT/dt$ is heating rate (^{0}K / Sec)

on intergrating both sides and substituting equation (4.2) for the TL intensity.

$$I = n_o' c s e^{- E/KT} \exp \int_0^T - \frac{s}{\beta} e^{- E/KT^1} dT^1 \qquad \text{---(4.3)}$$

n_o is the initial number of trapped electrons, At a fixed temperature T. $cse^{- E/KT}$ is a constant and is taken as λ, Equation (2) can thus be written as.

$$\frac{dn}{n} = -\lambda t$$

which on integration gives,

$$n = n_o e^{-\lambda t} \qquad \text{------ (4.4)}$$

equation (4.2) and (4.4.)

$$I = I_o \, e^{-\lambda t} \qquad (I_o = \lambda n_o) \text{ ---- (4.5)}$$

Thus at a fixed temperature T, TL intensity decays exponentially and TL process is said to be following first order kinetics.

4.2.3 : SECOND ORDER KINETICS OR GARLICK AND GIBSON'S THEORY :-

Garlick and Gibson considered the case, where a free electron has equal probability for go in to recombination centres or returning to the same trap (retrapping). If N is the total number of traps of which n are occupied at a time t, the probability that a released electron will go to the recombination centre is $\frac{n}{(N-n) + n} = \frac{n}{N}$

$$\text{Therefore} \quad I = c \frac{dn}{dt} \frac{n}{N}$$

$$= - c \, s \, e^{-E/KT} \, . \, \frac{n^2}{N} \qquad \text{-------} \; (4.6)$$

By integrating eq. (4.6) and rearranging equation for TL intensity is obtained as

$$I = \frac{no^2 \, c \, s^1 \, e^{-E/KT}}{\left(1 + s^1 \frac{no}{\beta} \int_0^T \exp (-E/KT^1) \, dT^1 \right)^2} \text{------} (4.7)$$

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

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

$$I = \frac{I_o}{(1 + \lambda^1 n_o t)^2}$$

Where $\lambda^1 = c \, s^1 e^{-E/KT}$ ------ (4.8)

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

4.2.4 : GENERAL ORDER KINETICS :

In many cases, a process follows neither the first order kinetics nor the second order kinetics. May and Partridge (41) gave a following equation which is applicable to a process following any non first order of kinetics.

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

$$= - c\, s' \, n^{L} \exp.\,(- E/KT) \text{ ----- } (9)$$

Where L is order of kinetics and can have any value not necessarily an integer solution of

$$I = S' n_o^{\,L} c \;\exp (- E/KT) \; \frac{(L-1)\, s' \,(n_o)^{L-1}}{\beta} \int_0^T \left[\exp (- E/KT') \, dT' + 1 \right]^{-L/L-1} \text{ --(4.10)}$$

$S' \, n_o^{\,L-1}$ has the unit (sec $)^{-1}$ and in this sense, it is similar to frequency factor S of the first order case. Thus equation (4.10) can be written as

$$I = cS\, n_o \exp (- E/KT) \; \frac{(L - 1)s}{\beta} \int_0^T \left[\exp (-E/KT') \, dT' + 1 \right]^{-L/L-1} \text{ ---(4.11)}$$

Eq^{n} (4.11) is not vali~~e~~d for L = 1 but when L → 1, it reduces to first order equation (4.3) and for L = 2 It reduces to second order equation (4.7)

TL intensity equation at a fixed temperature T can be derived as under.

From eqn (4.9), $\frac{dn}{n^L} = - S' e^{- E/KT} dt$

$$= - P' dt , \left[(P = S' e^{- E/KT}) \right]$$

Which on integration gives

$$n = (a + bt)^{\frac{1}{L-1}} \qquad \text{------(4.12)}$$

Where $a = (n_0)^{L-1}$ and $b = - P'' = - P' (L - 1)$

Substituting the values of n in (4.9) We get

$$I = - cp' (a + bt)^{\frac{1}{L-1}}$$

or $$I^{\frac{L-1}{L}} = (- cp')^{\frac{1}{L-1}} (a + bt) \qquad \text{----- (4.13)}$$

$$= A + Bt$$

Where $A = a (- cp')^{\frac{1}{L-1}}$ and $B = (- cp')^{\frac{1}{L-1}} . b$

Thus, if the TL process is following a general order kinetics, decay of TL intensity with time is governed by equation (4.13) such that plot of $(I)^{\frac{1}{L-1}}$ Vs time would give a straight line.

4.3 : Methods for determining the 'trap depth' :-

There exist several methods for determining the trap depth from the glow curves and these have been reviewed by Narlikar & Shalgaonkar (3). Using these methods, the trap depth E is estimated either from the peak temperature T_m or from the shape of the glow curve. These methods can be classified into two main types. i) Methods sensitive to the recombination kinetics and ii) Methods independent of the recombination kinetics.

A) Methods sensitive to the recombination kinetics

1) Randall and Wilkin's method :

Randall and Wilkin's (1) method is based on equation 4.5 which assumes monomolecular kinetics and no retrapping. In this method, Tm corresponds to a temperature a little below that at which the frequency of an electron escaping the trap is one per second, i.e.

$$S. \exp. (-E/KT_m) \; (1 + f (S, \beta) = 1 \qquad .... (4.14)$$

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

$$E = T_m (1+F (S.\beta) \;) K \log S \qquad .... (4.15)$$

Where F (S,B) is another function of S and β. When β lies between 0.5 and 2.5°K sec^{-1} and S equals the value 2.9 X $10^9 sec^{-1}$ the above equation reduces to

$$E = 25 \; K \; T_m \qquad ....(4.16)$$

2) Method due to Urbach :

Although the method due to Randall and Wilkins is earliest published method for determination of trap depth, Urbach (4) from equation 4.5 independently derived an expression for activation energy E by taking $S = 10^9 \; sec^{-1}$. The equation is

$$E = \frac{T_m}{500} \qquad .... (4.17)$$

3) Method due to Curie :

Following Randall and Wilkins, Curie (5) has given the formula for evaluation of trap depth as

$$E = \frac{T_m \; ({}^{o}k) \; - T_0 \; (\beta/ S)}{K \; (\cdot \beta/S \;)} \qquad .... (4.18)$$

where the functions T_0 and K may be obtained graphically for various sets of (β/S) with 1% accuracy (6,7,8).

It is worth noting that, there exist several other methods to determine which do not require the knowledge of S and hence equation which is obtained by differentiating equation 4.5 with respect to T and equating to zero may be useful (3,6,9) i.e.

$$\frac{E}{kT_m^2} = \frac{S}{\beta} \exp. \left(-E/KT_m \right) \qquad \text{....(4.19)}$$

4) Method due to Booth and Sohum :

Booth and Sohum (10,11) independently used two heating rates β_1 and β_2 and measured the corresponding values of T_{m_1} and T_{m_2} of the glow maximum. Solving the equation 4.14 for two different heating rates, they found,

$$E = \frac{kT_{m1}}{T_{m_1} - T_{m_2}} \log \frac{B_1 \; T_{m2}^2}{B_2 \; T_{m1}^2} \qquad \text{....(4.20)}$$

The value of S is given by (12)

$$\log \frac{S\ K}{E} = \frac{T_{m_2} \log \dfrac{T_{m2}^2}{\beta_2} - T_{m_1} \quad T_{m_1}^2/\beta_1}{T_{m_1} - T_{m_2}} \qquad \text{..(4.21)}$$

If T_m can be measured within an accuracy of 1°K, the method is found to yield E within an error of 5%.Schon (13) has modified the equation 4.15 by replacing T_m^2 by $T_m^{3.5}$ which has resulted in a some what improved accuracy.

5) 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. The method being isothermal has the advantage that such difficulties, as 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 can be analysed into sum of sharply defined linear region and it has been shown that for the first order kinetics.

$$I\ (T) = n_o\ S\ \exp.\ (\ -E/KT\ ).\ \exp.\ (S.t.\exp.\ (-E/KT\ ) \qquad \ldots(4.22)$$

Where t is the time. Taking logarithms of equation 4.17, we have

$$\log I\ (T) = -\ St\ \exp.\ (\ -E/KT\ ).\ \ -\ E/KT + \log n_o\ S \qquad \ldots(4.23)$$

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

$$m_1 = S.\ \exp.\ (\ -\ E/KT\ ) \qquad \ldots.(4.24)$$

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

$$\text{Log}\ \frac{m_1}{m_2} = \frac{(\ E\ )}{(\ K\ )}\ \left(\ \frac{1}{T_1} - \frac{1}{T_2}\ \right) \qquad \ldots\ (\ 4.25\ )$$

Which can be used to determine the activation energy E. The escape frequency factors may be found by the substitution of (4.25) in equation (4.24).

6) Method due to Grossweiner :

Using the equation 4.4 for the first order kinetics, Grossweiner (15) has shown that E in terms of T_m and T_1 is given by

$$E = \frac{1.51\ K\ T_m\ T_1}{(\ T_m - T_1\ )} \qquad \text{-----}\ (4.26)$$

Where T_1 is the temperature at which the low termperature side of the glow peak attains one half of the maximum intensity. According to Grossweiner this equation is accurate within ± 5% provided that $\frac{S}{\beta} > 10^7\ {}^oK^{-1}$ and $\frac{E}{kT_m} > 20$

However Dussel and Bube (16) and Chen (9) have shown that the equation 4.26 yields values which are about 7% higher if suitable modification is done.

7) Method using high temperature side glow peak (Method due to Lushchik) :

By assuming that the area of the half peak towards the fall off is equal to the area of a traingle having the same hight and half width, Luschchik (17) showed that the activation energy for the first order kinetics is given by

$$E = \frac{k T_m^2}{(T_2 - T_m)} \qquad \ldots(4.27)$$

under the same assumption, he obtained for the second order kinetics,

$$E = \frac{2K Tm^2}{(T_2 - T_m)} \qquad \ldots(4,28)$$

for better accuracy, the above two equations have been empirically modified by Chen (9) by multiplying by 0.978 and 0.853 for the first and second order kinetics respectively.

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

8) Method using Low temperature of the glow peak (Method due to Halperin & Braner)

In this method, the use of symmetry of the glow peak about its maximum is considered to calculate the activation energy. Halperin and Braner (18,19) considered the luminescence emission as mainly due to two kinds of recombination processes..

In one process, the electron raised to an axcited state with the forbidden gap below the conduction band recombenes with the hole by tunneling process and the other recombination takes place via conduction band. If it is assumed that the ratio ' ξ ' of the initial concentration of trapped electrons to trapped holes is close to unity, then the thermal activation energy E can be calculated using the appropriate equations given below :

Types of Process	Equation	Condition
Tunneling, = 1.		
a) Recombination dominant	$E_1 = \frac{KT_m^2}{(T_2 - T_m)}$	$\mu_g = e^{-1}$ --(4.29)
b) Retrapping dominent	$E_2 = \frac{2kt_m^2}{(T_2 - T_1)}$	$\mu_g = .5$ --- (4.30)
Via conduction band		
a) First order dominent	$E_3 = \frac{1.72\ KT_m^2}{(T_2 - T_1)}$	$(1-\underline{5.16})\ \mu_g\ e^{-1}(1 + \frac{2}{\Delta})$ --(4.31)
b) Second order dominant	$E_4 = \frac{2KT_m^2}{(T_2 - T_1)}$	$(1 - \frac{6}{\Delta})\ \mu_g \geqslant e^{-1}(1 + \frac{2}{\Delta})$ ---(4.32)

Where $\frac{1}{\Delta} = \left(\frac{KT_m}{E}\right) \ll 1$ is a correction factor and T_1 is the temperature on low temperature side of glow peak at which intensity is 1/2 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 characteristics of the type of kinetics involved in the process. The value of μ_g equal to or less than e^{-1} $(1 + \frac{2}{\Delta})$ should be obtained for first order process while values greater than e^{-1} is bimolecular. Thus the advantage of the method lies in the fact that the first half of the peak is sufficient for the evaluation of E and it also gives the direction for determing the kinetics involved in the process. But many times, the presence of weak shoulders at the high temp. side of the glow peak causes an apparent increases in the μ_g values which may wrongly indicate the process to be of the second order (20), when the ratio is greater than unity, the activation energy is given by,

$$E = \frac{KT_m^2}{(T_2 - T_m)} \left(1 + \frac{(T_2 - T_1)}{(T_m - T_1)} \right) \qquad \ldots.(4.33)$$

9) Method using to full half width of the glow peak (Method due to Chen)

The method suggested by Chen (9) to determine E follows from Randall and Wilkin's formula with the same assumption as made by Lushchik. For the first order kinetics E is given by

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

and for second order kinetics

$$E = 2\ KT_m \left(\frac{1.756\ T_m}{(T_2 - T_1)} - 1 \right) \qquad \ldots(4.35)$$

Here the numerical constants are chosen empirically to have a better estimation of E and $\frac{E}{KT_m} \gg 1$

Moreover Chen (21) showed that the symmetry factor, $\mu_g \simeq 0.42$ is characteristics of the first order peaks while $\mu_g \simeq 0.52$ of second order ones on correlating the symmetry factor μ_g and the order of kinetics, he gave the following equations to evaluate E for general order kinetics.

$$E_\tau = \left(1.51 + 3.0 (\mu_g - 0.42) \right) \frac{KT_m^2}{T_m - T_1} \qquad \ldots(4.36)$$

$$- \left(1.5 + 4.2 (\mu_g - 0.42) \right) . 2 KT_m$$

$$E_\delta = \left(0\text{-}976 + 7.3 (\mu_g - 0.42) \right) . \frac{KT_m^2}{T_2 - T_m} \qquad \ldots(4.37)$$

$$E_w = \left(2.52 + 10.2 (\mu_g - 0.42) \right) \frac{KT_m^2}{T_2 - T_1} - 2KT_m \qquad \ldots(4.38)$$

In addition to above, chen suggested corrections to the formulae suggested by the other workers which are as follows:

a) Chen's modification to method due to Grossweiner :

Chen modified the Grossweiner's relation (equation 4.26) empirically giving

$$E = \frac{C_1 k \, T_m \, T_1}{(T_m - T_1)} \qquad \ldots(4.39)$$

Where $C_1 = 1.41$ for first order kinetics and $C_1 = 1.60$ for second order, which gives E values with better accuracy over a wide range of S values (10^6 to 10^{13}sec^{-1}).

b) Chen's modification to method due to Luschik

Chen suggested that if area under the glow curve is not exactly equal to the area of a traingle approximated, then Luschik's method needs correction. Accordingly he gave the correction and the formula are

$$E = \frac{C_6 \; k \; T_m^2}{T_2 - T_m} \qquad \ldots\ldots(4.40)$$

With $C_6 = 0.976 \pm 0.004$ for first order kinetics and

$$E = \frac{C_7 2 \cdot k \cdot T_m^2}{T_2 - T_m} \qquad \ldots\ldots(4.41)$$

with $C_7 = 0.853 \pm 0.0012$ for second kinetics.

c) Chen's correction to method due to Halperin and Braner :

Applying some correction to method due to Halperin and Braner, Chen (9) suggested the equation for first order kinetics as

$$E_{H_1} = \frac{1.51 \; k \; T_m^2}{(T_m - T_1)} - (1.58 \times 2 \; k \; T_m) \qquad \ldots(4.42)$$

and for second order kinetics at

$$E_{H_2} = \frac{1.81 \; K \; T_m^2}{(T_m - T_1)} - (2 \; K \; T_m) \qquad \ldots(4.42)$$

10) Inflection point Method :

The method proposed by Land (22) makes the use of inflection temperature, T_1 of the glow curve for evaluating E. The inflection temperature is given by setting $(d^2 I / dT^2) = 0$. for the intensity temperature relation. The equation obtained for E is

$$E = \frac{K \; T_m \; T_1}{T_1 - T_m} \log \frac{A}{\frac{(T_1)^2}{T_m}} \qquad \ldots (4.43)$$

Where A = 0.77 and 2.66 respectively for $T_1 < T_m$ and $T_1 > T_m$ for the first order kinetics, and A = 0.24 and 3.43 respectively for $T_1 < T_m$ and $T_1 > T_m$ for second order kinetics. Thus by measuring T_1 and T_m, E can be calculated.

11) Method due to Nambi, Bapat and Ganguly :

Thermal activation energy can be determined by the emperical formula developed by Nambi and coworkers (23) for $CaSO_4$: RE phosphors. The relation between glow peak temperature T_m and activation energy E is given by

$$E = 3.12 \times 10^{-3}\, T_m - 0.23 \qquad ..(4.44)$$

B) Methods independent of the Recombination kinetics :

1) Method due to Hoogenstraaten :

Using equation 4.19 Hoogenstraaten (24) has show that the peak temperature T_m is related to E by the equation :

$$\log e \left(\frac{Tm^2}{\beta} \right) = \frac{E}{kT_m} + \log \frac{E}{SK} \qquad \ldots (4.45)$$

Thus the plot between $\log e\ (T_m^2 / \beta)$ versus $1/T_m$ is linear with a slope equal to E/K and making an intercept of log S K/E. Thus both E and S can be determined.

2) Initial Rise Method :

The method of initial rise, suggested by Garlick and Gibson (2) is based on the fact that for all types of the kinetics the intensity in the initial part of the glow curve can be expressed in the form

$$I = F . \exp (- E / kT) \qquad \ldots .(4.46)$$

F being a function of the 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 the glow curve, the equation 4.42 takes the form.

$$\log_e (I) = - E/kT + \text{constant} \qquad ....(4.47)$$

A plot of log I against 1/T should give a straight line and the slope of which yields the value of E.

3) Numerical kinetics Method :

This method of analysis (25) involves a numerical computation which proceeds in small arbitrary time steps. During each step the concentration of trapped charge, the carrier 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 giving the best least square fit to the experimental data.

4.3.1:Methods for determination of escape frequency factor :

From the basic theory of luminescence, the expression for probability (p) of escape off of a trapped electron from a trap is given as

$$P = S \exp (- E/kT).$$

Where k is Boltzman constant, T is the absolute temperature and E is the activation energy. The pre-exponential factor 'S';called frequency factor because of its dimensions denotes the number of attempts per second made by a trapped electron to escape off.

The value of S can be obtained from photoconductivity, phosphorescence decay, and thermoluminescence measurements. Several methods exists to determins S from TL studies and a brief survey is given below.

1) Method due to Randall and Wilkins :

Randall and Wilkins (1) for the first order kinetics, have given the solution of general equation $I = \frac{-dn}{dt}$ with a constant heating rate β as

$$I = Sn_o \exp. (-E/kT) \exp. (- \frac{S}{\beta}) \int_T^{To} \exp.(-E/kT')dT' \qquad ...(4.48)$$

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

$$E / kT_m^2 = \frac{S}{\beta} \exp. (- E/KT_m) \qquad ....(4.49)$$

Where T_m is the temperature at the maximum of glow peak knowing T_m, β and E (determined by other methods) S can be readily evaluated.

2) Method due to Garlick and Gibson :

Following the second order kinetics, the solution of equation $I = \frac{-dn}{dt}$ given by Garlick and Gibson (2) with constant heating rate β is

$$I = S' \; n_o^2 \; \exp. (- E/kT). \left[1 + \left(\frac{S' \; n_o}{\beta} \right) \int_{T_o}^{T} \exp. (- E/kT') \; dT \right]^{-2} \qquad ....(4.50)$$

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

$$1 + \frac{(S' n_o)}{\beta} \int_{T_o}^{T_m} \exp.(-E/kT)\, dT = 2 \frac{kT_m^2}{\beta E} S' n_o \exp.(-E/kT_m) \qquad \ldots\ldots(4.51)$$

Assuming T_m to be the experimental peak temperature and with all other parameters in equation (4.51) are known, one can calculate the escape frequency factor $S = S'\ n_o$ for different values of E.

3) Isothermal Decay Method :

The method suggested by Gralick (14) for the first order kinetics points that in an isothermal decay, a plot of log I versus t may be regarded as a sum of sharply defined linear regions of slope m given by the equation.

$$S = m \exp.(E/kT) \qquad \ldots(4.52)$$

4) Method due to Curie :

As suggested by Curie (5), the glow peak temperature T_m and heating rate β are related to escape frequency factor by the equation of the type,

$$\frac{S}{\beta} = \frac{2}{\delta} \exp. \frac{2\,T_m}{\delta} \qquad \ldots.(4.53)$$

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 calculated.

5) Method due to Aramu and Maxia :

The method due to Aramu and Maxia (32) starts from the kinetic equation and allows to determine the frequency factor by the use of simplified formula.

$$S = \beta \exp. \eta \qquad \ldots(4.54)$$

Where β is heating rate and η is the intercept with the vertical axis of the plot of In I versus $1/_T$. The formula is applicable for the saturated glow peak and when the concentration of holes bound to luminescence centres is equal to the trapped electron concentration.

4.32 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 (33) proposed the following equation, on the assumption that the density of free electrons (or holes in case of hole traps) is equal to the density of empty traps.

$$\frac{1/\tau}{\sigma} = \frac{2\pi m \ (kT)^2}{h^3} \sqrt{6\pi} \ \exp.(- E/KT) \qquad ...(4.55)$$

on combining this equation with equation

$$P = \frac{1}{\tau} = S \exp.(- E/KT)$$ We have a numerical equation of the type

$$\sigma = \frac{S}{1.63 \times 10^{21} \times T^2} \qquad ....(4.60)$$

Which in its simplest form be given as (3)

$$\frac{S}{\sigma} = 1.5 \times 10^{26} \qquad ....(4.56)$$

Knowing S, value of 6 can be estimated approximately.

4.4 RESULTS AND DISCUSSION :

Samples are prepared with Nd; Sm; Tb; Dy keeping fixed % of atom in the host material (Sample no. KD_2, KD_3, KD_4, KD_5 resply). To see the starting çontribution in the host material it is also prepared KD_1 (CaS undoped) with out adding impurities. Fig. 4.2. shows the glow curves of the prepared samples it indicates that Dy, Sm, Tb and Nd are suitable (in descending order) as activator in the host material. fig. (4.2) exibits that there are few impurities introduced in the host material as starting contribution.

The samples KD (6) , CaS : Tb:Nd, KD(7) CaS : Nd : Sm. KD(8) CaS :Tb:Sm and (KD, (9) CaS:Dy:Tb are prepared by keeping fixed % of atom for these samples to find best activator and second activator in the host material by visual inspection after uv excitation. It is found that RE_1: RE_2 i.e. Sm :Nd and Dy:Tb are suitable inthe host material.

4.5.1: Results obtained when samples were excited by uV source for 200 seconds :

a) Glow Curve :- Glow curves for various samples with different concentrations of (Sm, Nd) and (Dy, Tb) are shown in fig. (4.3 - 4.6) and fig. (4.7 - 4.10) respectively. The heating rate used forrecording all glow curves is 2° c/Sec. The measurements have been carried out in the temperature range of 27°c to 390° c . The temperature programmer fabricated in the department is used for linear heating. Fig. 4.1 shows temperature profile of the instrument.

As seen from the graphs fig. (4.3 - 4.6) a single broad peak at around $105^{\circ}c$ is observed for all CaS :Sm :Nd phosphors, whereas two broad peaks are observed first broad peaks around $105^{\circ}c$ and second broad peak around $190^{\circ}c$ for all CaS :Dy :Nd phosphors, From the shape of glow curves it seems that the peak temperature slightly changes with concentration of activator Sm: Dy and second activator Nd : Tb in phosphors CaS :Sm :Nd and CaS :Dy :Tb respectively. The shift in peak temperature indicates that an apperent broad peak for all the phosphors, may be a composite peak having more than one peak and that these peaks are situated close to each other. Their resultant is indicated by a composite glow curve. In present study however the [illegible] peaks are not resolved using partial bleaching technique. Calculations of activation energies are done assuming the peak to be single.

It is observed that over all shape of the glow curves is not significantly affected by concentration variation of activator and co-activator for all phosphors of composition CaS : Sm : Nd. The peak structure and peak temperature are however different for Cas:Dy:Tb . Only the peak intensity changes with concentration fig. (4.11 - 4.12) show the variation of peak intensity with concentration for phosphors CaS:Sm:Nd and CaS:Dy:Tb respectively. From these graphs it is seen that peak intensity increases and again decreases with concentration of activator and second activator. The variation of peak temperature and peak intensity is given in table 4.1 and 4.2.

From graphs fig. (4.11 - 4.12) it is seen that the phosphors $CaS:Sm_{.02\%}:Nd_{.02\%}$ and $CaS:Dy_{.0075\%}:Tb_{.02\%}$ gives maximum TL out put amongst choosen concentration by atom percentage. Most suitable combination of RE_1 and RE_2 in the host material is seems is to be Dy:Tb.

b) Activation Energy :

Activation energy E, of glow peak can be evaluated by several ways as described in section 4.2. In present study activation energies are calculated from the shape of the glow curve by using different formulae due to (i) Urbach (ii) Luschik (iii) Halperin and Branner (iv) Chen (v) Gross Weiner. Values of E calculated using different formulae are in agreement. Table (4.4 - 4.5).

An attempt is also made to find the activation energy by initial rise method for sample KD 31, Typical Arrhenius plots are shown in fig. (4.13). The activation energy calculated by this method is .46(eV) which is also in good agreement with the energies calculated by other methods.

c) Variation of activation energy with concentration :

Tables (4.4, 4.5) show that activation energy does not vary significantly with concentration. The effective trap levels are distributed over a range of .60 ev to .67ev for Cas :Sm:Nd phosphors and .36 ev to .67 for first peak and .44 to .78 for second peak for Cas:Dy:Tb phosphors. The observed variation in both cases is not systematic. This suggests that the addition of activator, second activator does not introduce any new traps but only modifies the relative importance of trap in Case of Cas:Sm:Nd, but are probably responsible for different traps in Cas:Dy:Tb for thermoluminescence. (22,23)

d) Kinetics of Thermoluminescence :

From the shape of the glow curve, nature of the kinetics involved in the TL process can be determined by knowing summetry factor $\mu g = \delta / w$. The values of μg are listed in table (4.4, 4.5) for all samples. If $\mu g > e^{-1} (1 + \frac{2}{\Delta})$ then the kinetics involved in TL process is second order. From table (4.4, 4.5) $\mu g > e^{-1} \left[\frac{2}{\Delta} < 1 \right]$ for all the prepared samples which shows that kinetics involved for all in TL process may be second order.

Above statement is also supported by equation (4.8). A plot of '$1/\sqrt{I}$' versus 't' in isothermal decay is a straight line, hence kinetics involved in TL process should be bimolecular. Plots of $1/\sqrt{I}$ Versus t fig. (4.14) for the samples KD 21 & KD 31 shows straight line for isothermal decay at temperature 100°c and 250°c resply. It is explicit that TL process involved for all samples is bimolecular.

e) Escape frequency factor :

The escape frequency factor 'S' is calculated by using equation (4.49). The value of S depends on E So there is large variation of S for small change of E. The S values are estimated by taking activation energies obtained from Urbach formula. Which are listed in table (4.8) for all samples.

f) Size of trap (σ)

The capture cross section (σ) of each type of trapping centre can be evaluted from the knowledge of escape frequency factor. The values of σ are estimated by using equation (4.56) The values are listed in table (4.8). The size of the trap is of the order of 10^{-18} cm^2 . Thus the trap in present investigation may be regarded as medium size trap.

g) Dose dependence :

The intensity of glow peak is found to be a function of irradiation dose. The plot of the glow peak intensity against duration of excitation, known as " Build-up curve " is shown in figure (4.15, 4.16) for the samples KD 21. The intensity of glow peak initially increases gradually and then saturates under uv excitation of 45 minutes.

4.5.2: A) Results obtained when excitation source used is Co (60) gamma source (dose of 4000 R/ minute for duration of 30 minutes).

The TL glow curve of the samples excited by gamma irradiation (4000 R/minute) are shown in fig.(4.17 - 4.19) The heating rate used is 2°c/sec. The measurement have been carried out in the temperature range of 27°c to 390°c . The glow curves are recorded 92 days after gamma irradiation. All the glow curves exhibited three peaks first around 155°c, second around 205°c and third peak around 260°c . The peak around 205°c is dominent for all prepared phosphors. Peak around 105°c observed in u.v. excited phosphors is missing which is probably due to (room temperature) decay at low temperature. 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 deeper traps which favour high temperature peaks. The observation how ever requires persual.

General shape of the glow peak is same for all phosphors (CaS : Sm : Nd , CaS : Dy:Tb) . The peak temperature for first, second and third peak is also constant for all samples. The peak intensity changes with activator concentration However the change is not systematic (table 4.3) it is difficult to arrive at a systematic conclusion regarding concentration variation and TL out put.

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 u.v. excited and its TL was recorded. The shape of glow curve, peak temperature and peak intensity remains unaffected.

B) Activation energy :

In present study activation energies for peaks (155°c, 205°c and 260°c) are calculated by Urbach formula, table(4.7) for all prepared phosphors. From table (4.7) it is observed that activation energies for a peak (155°c or 205°c or 260°c) almost remain constant for all samples. These activation energies are higher than those obtained for u.v. excited sample by using same formula table (4.4, 4.5). This shows that there are deeper traps also introduced in the samples.

C) Kinetics of the luminescence :

The kinetics involved in TL is determined by calculating the value of symmetry factor (μ_g). It is observed that μ_g is grater than 1/e (table 4.7) . Which indicates that order of kinetics may be second order.

d) Escape frequency factor :

The escape frequency factor 'S' is evaluated by using equation (4.49). The values of S calcualated are listed in table (4.7) and are in the range of 10^9 sec^{-1} for variation in activator concentration.

e) Size of trap :

The size of trap is calculated by using equation (4.56). The values are listed in table (4.7). The size of the trap is of the order of 10^{-18} cm^2. The traps may be regarded as medium size trap.

4.6 SUMMERY :-

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

1) Shape of the glow curves mainly depends on the concentration of activator RE_1 and second activator RE_2 . The relative peak intensities are significantly influenced by RE_1 and RE_2 .

2) Addition of activators do not give rise to new glow peak in the temperature range studied.

3) The trap depths of effective levels are insensitive to the concentration of activators RE_1 and RE_2 .

4) The probable kinetics involved in TL process is of second order (bimolecular).

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

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TABLE No.4.1

PEAK TEMPERATURE °K AND PEAK TL INTENSITY (ARBUNIT) FOR THE PHOSPHORS CaS:Sm:Nd EXCITED UNDER ULTRAVIOLET SOURCE :

% variation of Sm.			% Variation of Nd		
Sample No.	Peak Temp.	Peak TL intensity	Sample No.	Peak Temp.	Peak TL Intensity
KD 13	393	470	KD20	383	1400
KD 14	383	1700	KD21	383	2400
KD 15	383	950	KD22	393	2300
KD 16	365	1600	KD23	383	800
KD 17	393	650	KD24	383	1850
KD 18	387	620	KD25	373	1800
KD 19	393	230	KD26	351	550
			KD27	357	175
			KD28	323	90

TABLE No. 4.2

PEAK TEMPERATURE °K AND PEAK INTENSITY (IN Arb. UNITS) FOR THE PHOSPHORS CaS:Dy:Tb EXCITED UNDER ULTRA VIOLET SOURCE :

Sample No.	% Variation of Dy.			
	Peak I		Peak II	
	Peak Temperature °K	Peak TL intensity	Peak Temperature °K	Peak TL intensity
KD29	337	560	453	760
KD30	341	800	435	670
KD31	373	1100	423	1400
KD32	333	500	393	440
KD33	343	255	423	165
KD34	343	150	443	115
KD35	335	220	443	80
KD36	343	85	435	67
KD37	327	54	443	28
KD38	337	200	423	70
KD39	343	130	-	-
KD40	339	65	423	25

Sample No.	% Variation of Nd			
	Peak I		Peak II	
	Peak temp. °K	Peak TL intensity	Peak temp. °K	Peak TL intensity
KD41	343	323	435	90
KD42	343	700	435	510
KD43	343	360	435	135
KD44	343	415	435	150

TABLE No. 4.3

PEAK TEMPERATURE IN ^{o}K AND PEAK INTENSITY IN Arb. UNIT FOR THE PHOSPHERS UNDER γ - IRRADIATION SOURCE

Sample No.	Peak I		Peak II		Peak III	
	Peak Temp.	Peak TL intensity	Peak Temp.	Peak TL Intensity	Peak Temp.	Peak TL intensity
	CaS:Sm:Nd % variation of Sm					
KD13	413	31	-	-	523	500
KD14	413	76	453	8500	543	990
KD15	-	-	-	-	--	-
KD16	-	-	-	-	-	-
KD17	433	78	453	1200	533	50
KD18	413	25	453	180	523	45
KD19	-	-	-	-	543	60
	CaS:Sm:Nd % variation of Nd					
Kd20	413	130	453	120	533	115
KD21	353	250	433	140	-	-
KD22	413	150	453	920	543	100
KD23	413	120	453	120	513	270
KD24	413	100	453	400	-	-
KD25	413	120	473	320	543	82
KD26	413	155	453	700	543	300
KD27	-	-	453	1100	-	-
KD28	-	-	453	1100	553	150
	CaS:Dy:Nd % variation of Dy					
KD32	-	-	453	300	563	100
KD33	-	-	473	140	-	-
KD34	-	-	453	400	563	32
KD35	-	-	473	345	563	24
KD36	413	20	473	1100	553	70
KD37	-	-	453	800	553	120
KD38	413	60	453	8000	563	85
KD39	413	48	-	-	543	18
KD40	413	20	453	30	543	22

TABLE NO. 4.4

ACTIVATION ENERGY SYMMETRY FACTOR FOR ULTRAVIOLET EXCITED CaS.Sm:Nd, samples using different formulae in eV

EU : Energy due to Urbach.
EL : Energy due to Lushchik.
E_{Lc} : Energy due to Luschik and Chen's modification.
Ec : Energy due to Chen.
E_{HBC}: Energy due to Halperin and Braner withChen's modification.
E_{CG} : Energy due to Gross weiner with Chen's modification.

Sample No.	μg	E_U	E_L	E_{Lc}	E_{HBc}	E_{CG}	E_c
KD13	.78	.788	.48	.40	.46	.41	.78
KD14	.45	.76	.70	.59	.44	.41	1.10
KD15	.62	.73	.49	.41	.68	.63	.81
KD16	.40	.76	.50	.42	.50	.47	1.70
KD17	.43	.78	.84	.71	.34	.38	1.73
KD18	.53	.77	1.12	.95	.83	1.02	1.75
KD19	.38	.78	.95	.81	1.029	.80	1.4
KD20	.43	.766	.66	.56	.39	.36	.8
KD21	.42	.766	.90	.76	.538	.50	1.10
KD22	.42	.78	.88	.75	.53	.50	1.1
KD23	.59	.76	.60	.51	.48	.34	.99
KD24	.43	.76	.63	.53	.37	.35	.78
KD25	.41	.74	.92	.78	.54	.50	1.1
KD26	.52	.74	.53	.45	.47	.45	.87
KD27	.58	.71	.64	.54	.76	.71	1.07
KD28	.64	.64	.54	.44	.67	.64	.73

TABLE No.4.5

ACTIVATION ENERGY (Symmetry factor) FOR ULTRAVIOLET EXCITED. CaS:Dy:Tb SAMPLES FOR FIRST PEAK USING DIFFERENT FORMULAE IN eV :

Sample No.	μ_g	E_U	E_L	E_{Lc}	E_{HBC}	E_{CG}	E_C
KD29	.79	.64	.42	.36	1.30	1.30	.68
KD30	.80	.67	.30	.26	1.00	1.00	.47
KD31	.42	.68	.39	.39	.35	.37	.43
KD32	.84	.74	.31	.27	1.06	1.55	.50
KD33	.64	.66	.40	.34	.59	.55	.65
KD34	.65	.68	.44	.37	.70	.66	.71
KD35	.77	.68	.40	.34	.73	.70	.65
KD36	.59	.67	.63	.54	.77	.72	1.05
KD37	.92	.68	.38	.32	-	-	.61
KD38	.69	.65	.54	.46	1.0	.97	.89
KD39	.48	.67	.39	.38	.45	.46	.91
KD40	.70	.68	.41	.35	.84	.78	.66
KD41	.71	.726	.45	.38	.96	.9	.73
KD42	.51	.76	.90	.76	.81	.76	.67
KD43	.91	.69	.32	.27	. 6	.9	.67
KD44	.62	.73	.58	.49	.81	.76	.95

TABLE No.4.6

ACTIVATION ENERGY (Symmetry factor) ULTRAVIOLET EXCITED SAMPLE CaS:Dy:Tb FOR SECOND PEAK IN eV

Sample No.	μ_g	E_U	E_L	E_{Lc}	E_{HBc}	E_{CG}	E_c
KD29	.50	.90	.61	.52	.49	.46	.99
KD30	.43	.87	.28	.28	.30	.34	.62
KD31	.58	.84	.48	.41	.53	.44	.77
KD32	.59	.78	.41	.36	.48	.45	.66
KD33	.64	.84	.52	.45	.86	.80	.84
KD34	.43	.88	.34	.36	.37	.37	.76
KD35	.44	.88	.34	.36	.36	.38	.76
KD36	.49	.87	.27	.27	.30	.34	.61
KD37	.55	.87	.44	.37	.49	.45	.70
KD38	.56	.87	.46	.39	.48	.45	.74
KD39	-	-	-	-			
KD40	.56	.84	.44	.39	.48	.44	.75
KD41	.45	.866	.78	.66	.64	.59	1.30
KD42	.2	.866	-	-	-	-	-

TABLE : 4.7 :- ACTIVATION ENERGY, FREQUENCY FACTOR (FROM EU) AND SIZE OF TRAP FOR THE SAMPLES IRRADIATED UNDER y - SOURCE

E --- ACTIVATION ENERGY (eV), S - FREQUENCY FACTOR Sec^{-1} , - SIZE OF TRAP (Cm^{2}) :

Sample	First peak			Second peak			Third peak		
No.	E	S	σ	E	S	σ	E	S	σ
1	2	3	4	5	6	7	8	9	10
KD 13	.84	2.1x10^{9}	1.3x10^{-17}	-	-	-	1.04	9x10^{8}	5.7x10^{-18}
KD 14	.82	1.1x10^{9}	7.0x10^{-18}	.94	2.9x10^{9}	1.8x10^{-17}	1.08	8.8x10^{8}	5.6x10-^{18}
KD 15	-	-	-	-	-	-	-	-	-
KD 16	-	-	-	-	-	-	-	-	-
KD 17	.86	1.06x10^{9}	6.7x10^{-18}	.94	2.9x10^{9}	1.8x10^{-17}	1.04	8.9x10^{8}	8.5x10^{-18}
KD 18	.84	2.1x10^{9}	1.3x10^{-17}	.94	2.9x10^{9}	1.8x10^{-17}	1.04	8.9x10^{8}	8.5x10^{-18}
KD 19				.87	1.4x10^{9}	8.9x10^{-17}	1.08	8.8x10^{8}	5.6x10^{-18}
KD 20	.84	2.1x10^{9}	1.3x10^{-17}	.94	2.9x10^{9}	8.9x10^{-17}			
KD 21	.72	2.5x10^{9}	1.6x10^{-17}	.85	1.4x10^{9}	8.9x10^{-17}	1.066	8.9x10^{8}	8.6x10^{-18}
KD 22	.84	2.1x10^{9}	1.3x10^{-17}	.94	2.9x10^{9}	1.8x10^{-17}	1.08	8.8x10^{8}	5.6x10^{-18}
K 23	.86	1.06x10^{9}	6.7x10^{-18}	-	-	-	1.02	9.2x10^{8}	5.8x10^{-18}
KD 24	.84	2.1x10^{9}	1.3x10^{-17}	.94	2.9x10^{9}	1.8x10^{-17}	-	-	-
KD 25	.86	1.06x10^{9}	1.3x10^{-17}	.96	1.6x10^{9}	1.02x10^{-17}	1.08	8.8x10^{8}	5.6x10^{-18}

contd...next page

TABLE : 4.7-Contd....

1	2	3	4	5	6	7	8	9	10
KD 26	.84	$2.1x10^9$	$1.3x10^{-17}$	.94	$2.9x10^9$	$1.8x10^{-17}$	1.08	$8.8x10^8$	$5.6x10^{-18}$
KD 27	-	-	-	.94	$2.9x10^9$	$1.8x10^{-17}$	-	-	-
KD 28	-	-	-	.94	$2.9x10^9$	$1.8x10^{-17}$	1.1	$8.5x10^8$	$5.5x10^{-18}$
KD 32	-	-	-	.94	$2.9x10^9$	$1.8x10^{-17}$	1.12	$8.5x10^8$	$5.4x10^{-18}$
KD 33	-	-	-	.96	$1.6x10^9$	$1.02x10^{-17}$	-	-	-
KD 34	-	-	-	.94	$2.9x10^9$	$1.8x10^{-17}$	1.12	$8.5x10^8$	$5.4x10^{-18}$
KD 35	-	-	-	.96	$1.6x10^9$	$1.02x10^{-17}$	1.12	$8.5x10^8$	$5.4x10^{-18}$
KD 36	.84	$2.1x10^9$	$1.3x10^{-17}$	.96	$1.5x10^9$	$1.02x10^{-17}$	1.1	$8.6x10^8$	$5.5x10^{-18}$
KD 37	-	-	-	.94	$2.9x10^9$	$1.8x10^{-17}$	1.1	$8.6x10^9$	$5.5x10^{-18}$
KD 38	.84	$2.1x10^9$	$1.3x10^{-17}$	.94	$2.9x10^9$	$1.8x10^{-17}$	1.12	$8.5x10^8$	$5.4x10^{-18}$
KD 39	.84	$2.1x10^9$	$1.3x10^{-17}$	-	-	-	1.08	$8.8x10^8$	$5.6x10^{-18}$
KD 40	.84	$2.1x10^9$	$1.3x10^{-17}$	.94	$2.9x10^9$	$1.8x10^{-17}$	1.08	$8.8x10^8$	$5.6x10^{-18}$

TABLE No.4.8 : ESCAPE FREQUENCY FACTOR (Using E_y) AND SIZE OF TRAP EXCITED SAMPLES UNDER uv :

Sample No.	Peak I		Peak II	
	S_{Sec}^{1}	σ $(Cm)^2$	S_{Sec}^{-1}	σ $(Cm)^2$
KD13	$1.38x10^9$	$8x10^{-18}$		
KD14	$1.42x10^9$	$9.1x10^{-18}$		
KD15	$1.42x10^9$	$9.1x10^{-18}$		
KD16	$1.48x10^9$	$9.1x10^{-18}$		
KD17	$1.38x10^9$	$9.48x10^{-18}$		
KD18	$1.42x10^9$	$9.1x10^{-18}$		
KD19	$1.42x10^9$	$8.84x10^{-18}$		
KD20	$1.38x10^9$	$9.1x10^{-18}$		
KD21	$1.42x10^9$	$9.1x10^{-18}$		
KD22	$1.38x10^9$	$8.84x10^{-18}$		
KD23	$1.42x10^9$	$9.1x10^{-18}$		
KD24	$1.42x10^9$	$9.1x10^{-18}$		
KD25	$1.28x10^9$	$8.2x10^{-18}$		
KD26	$2.35x10^9$	$1.5x10^{-17}$		
KD27	$1.52x10^9$	$9.74x10^{-18}$		
KD28	$1.68x10^9$	$1.07x10^{-17}$		
KD29	$1.46x10^9$	$9.73x10^{-18}$	$1.28x10^9$	$8.53x10^{-18}$
KD30	$1.6x10^9$	$1.06x10^{-17}$	$1.25x10^9$	$8.33x10^{-18}$
KD31	$1.06x10^9$	$1.06x10^{-17}$	$1.2x10^9$	$8x10^{-18}$
KD32	$1.63x10^9$	$1.07x10^{-17}$	$1.38x10^9$	$9.2x10^{-18}$
KD33	$1.59x10^9$	$1.06x10^{-17}$	$1.2x10^9$	$8x10^{-18}$
KD34	$1.52x10^9$	$1.06x10^{-17}$	$1.23x10^9$	$8.2x10^{-18}$
KD35	$1.62x10^9$	$1.08x10^{-17}$	$1.23x10^9$	$8.2x10^{-18}$
KD36	$1.59x10^9$	$1.06x10^{-17}$	$1.25x10^9$	$8.33x10^{-18}$
KD37	$1.66x10^9$	$1.1x10^{-17}$	$1.23x10^9$	$8.2x10^{-18}$
KD38	$1.46x10^9$	$9.7x10^{-18}$	$4.2x10^9$	$8x10^{-18}$
KD39	$1.59x10^9$	$1.06x10^{-17}$	-	-
KD 40	$1.49x10^9$	$9.93x10^{-18}$	$5.08x10^{10}$	$8x10^{-18}$
KD41	$1.5x10^9$	9.7×10^{-18}	-	-
KD42	$1.42x10^9$	9.1×10^{-18}	-	-
KD43	$5.9x10^8$	3.9×10^{-18}	-	-
KD44	$1.48x10^9$	9.1×10^{-18}	-	-

TEMPERATURE PROFILE OF LINEAR TEMPERATURE PROGRAMMER

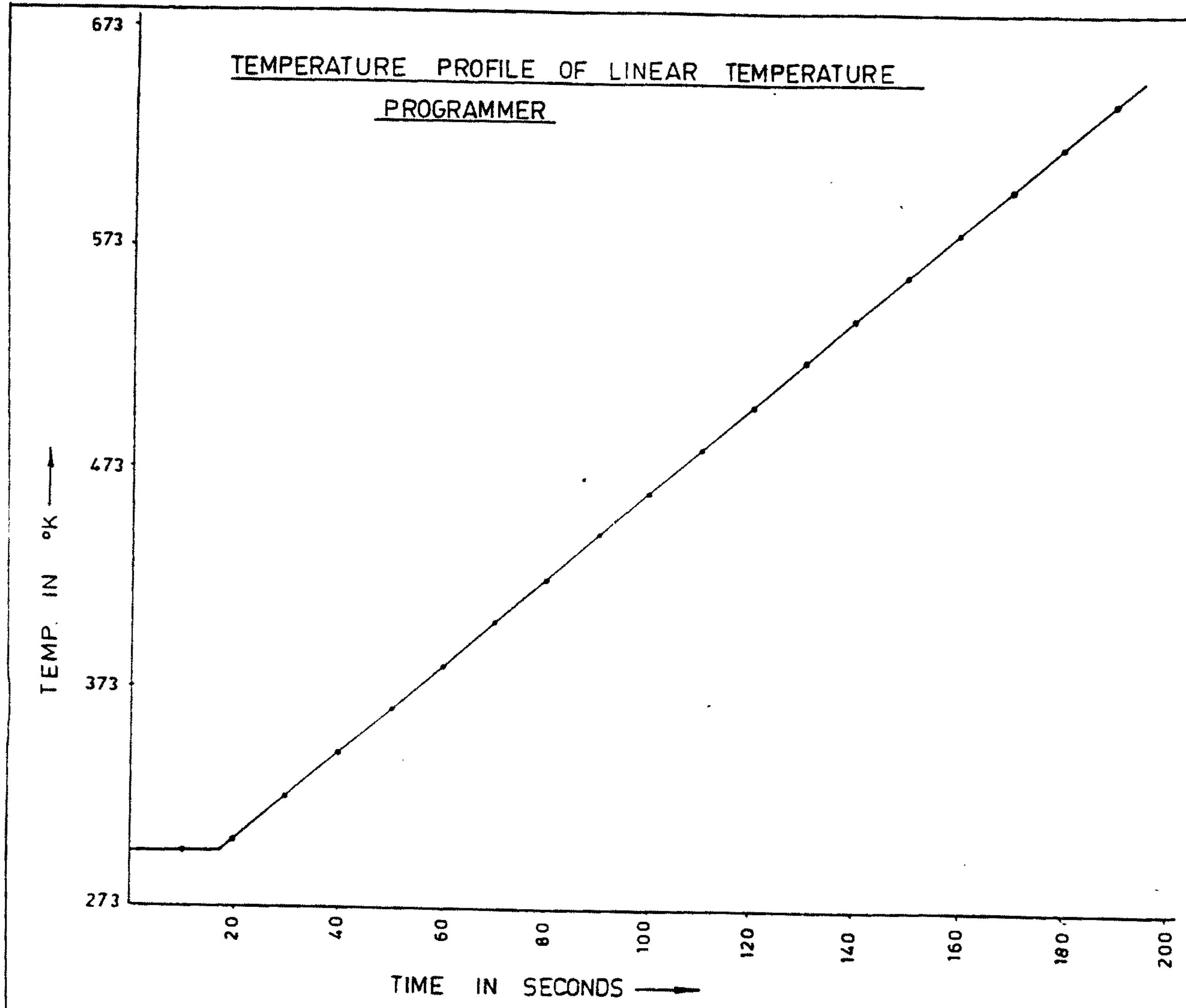
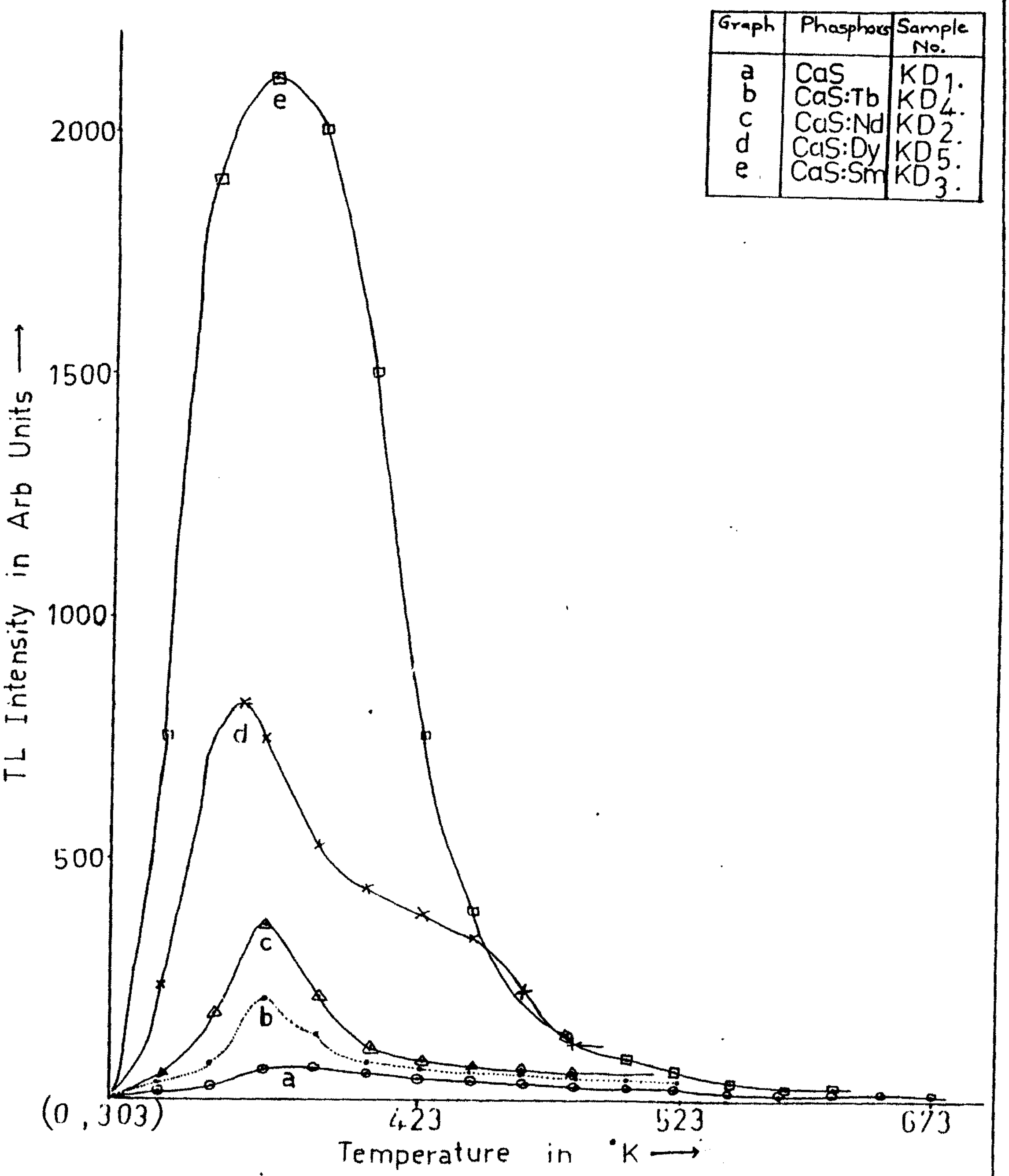


FIG. NO.- 4·1



PLOTS OF TL INTENSITY Vs TEMP.

FIG.NO.: 4·2.

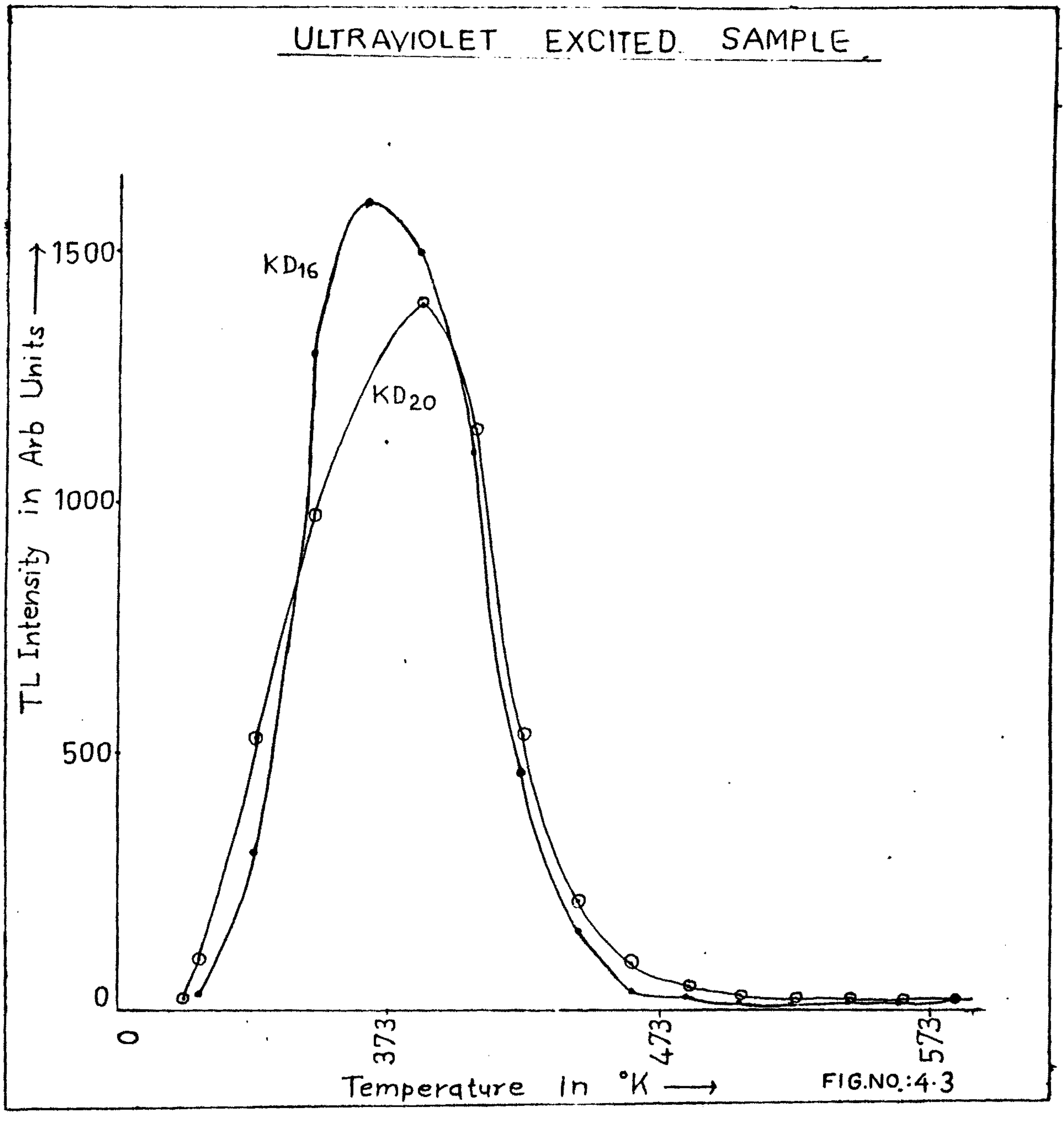
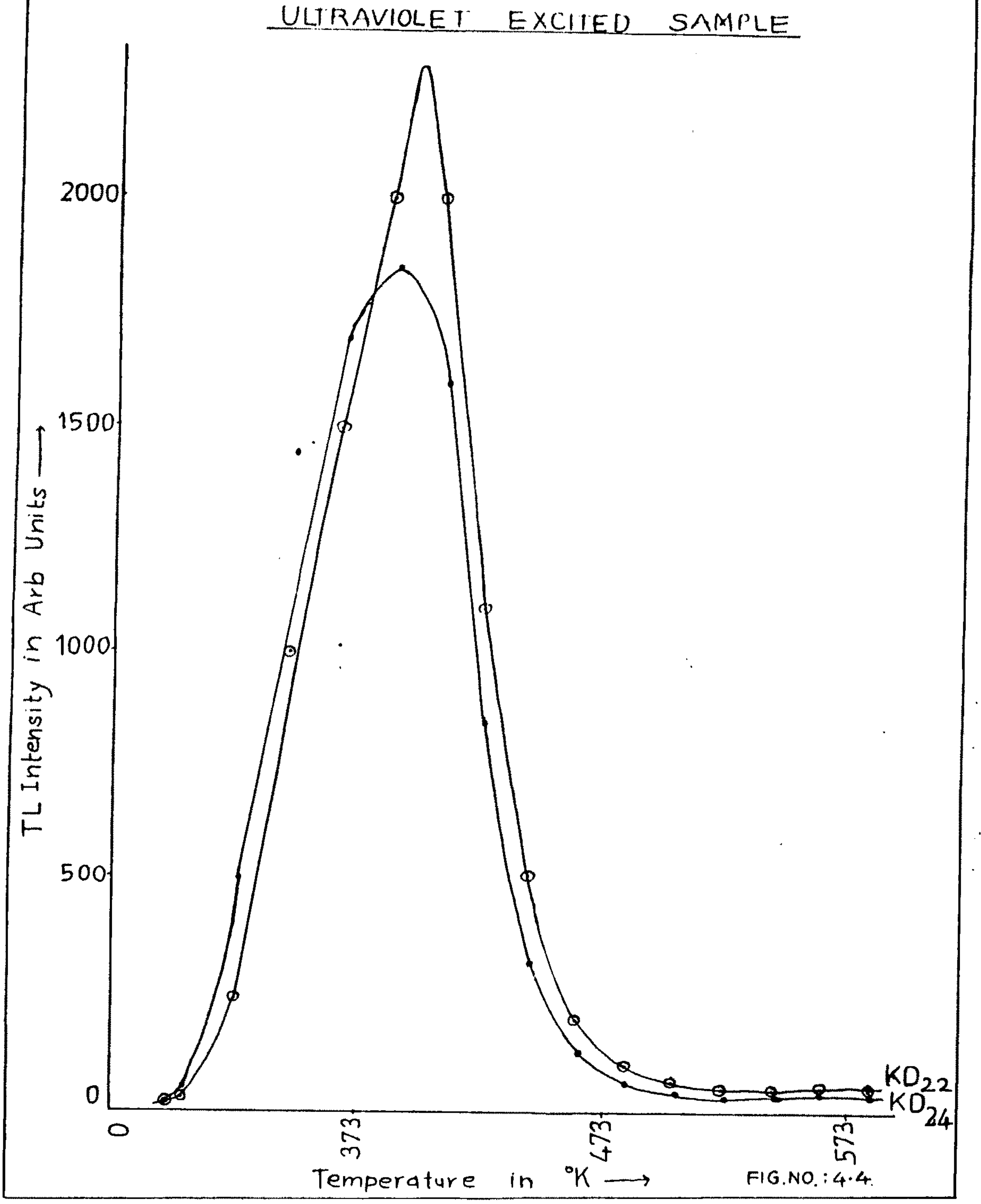

ULTRAVIOLET EXCITED SAMPLE
KD16
KD20
TL Intensity in Arb Units
1500
1000
500
0
0
373
473
573
Temperature In °K

FIG.NO.:4.3



ULTRAVIOLET EXCITED SAMPLE

FIG.NO.: 4·4.

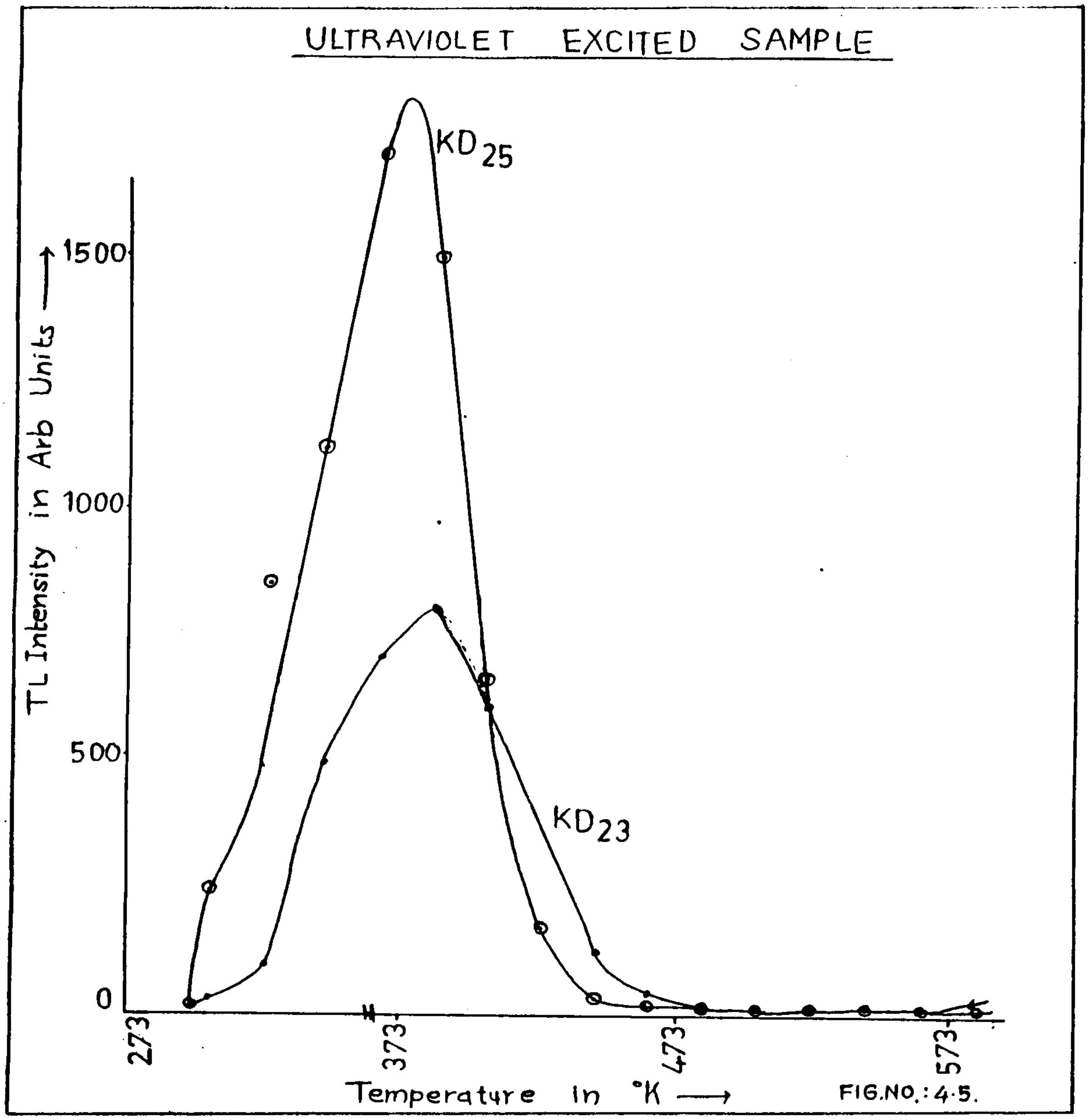

ULTRAVIOLET EXCITED SAMPLE
KD$_{25}$
KD$_{23}$
TL Intensity in Arb Units →
1500
1000
500
0
273
373
473
573
Temperature in °K →

FIG.NO.: 4·5.

ULTRAVIOLET EXCITED SAMPLE

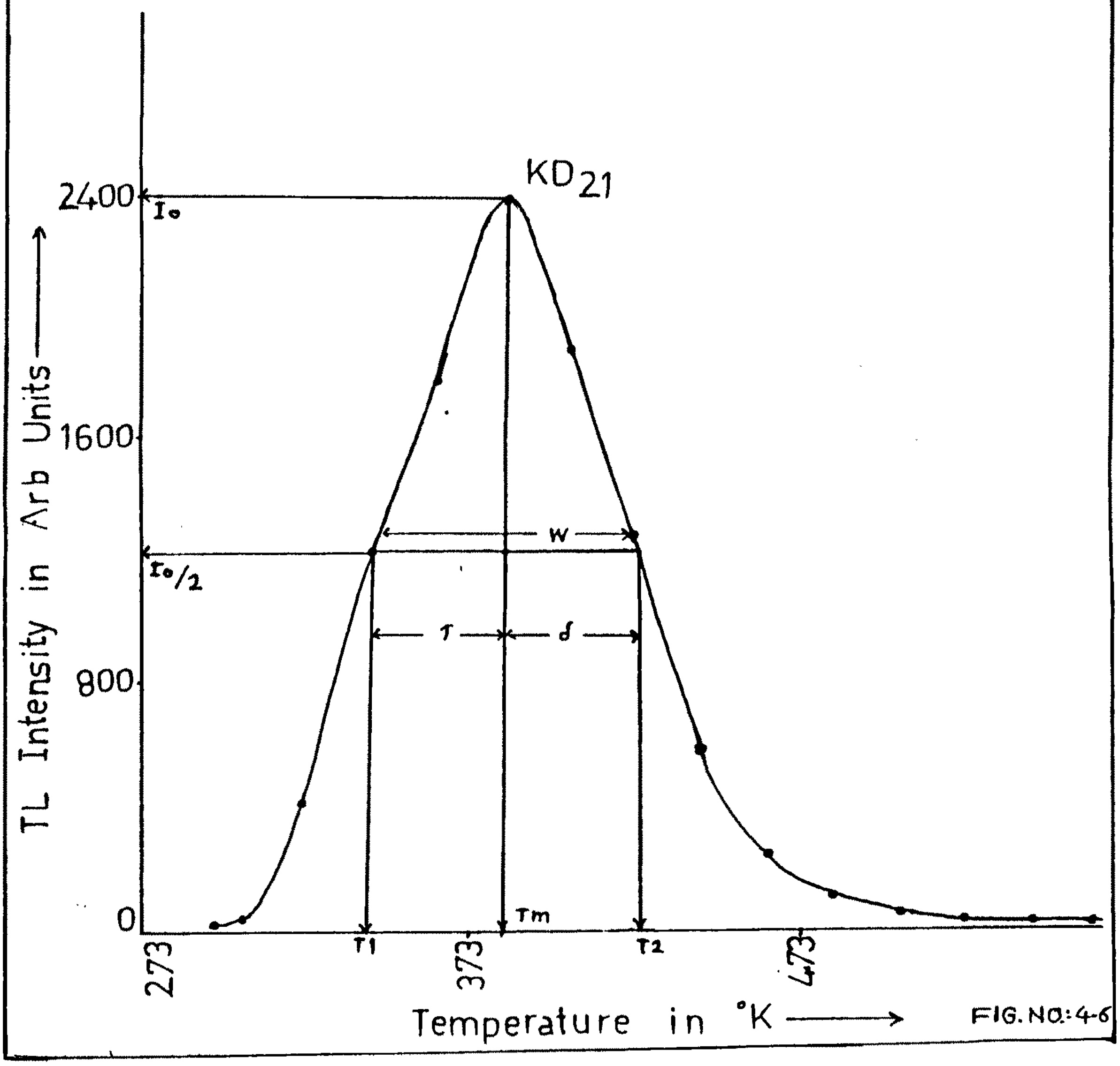


FIG. NO: 4-6

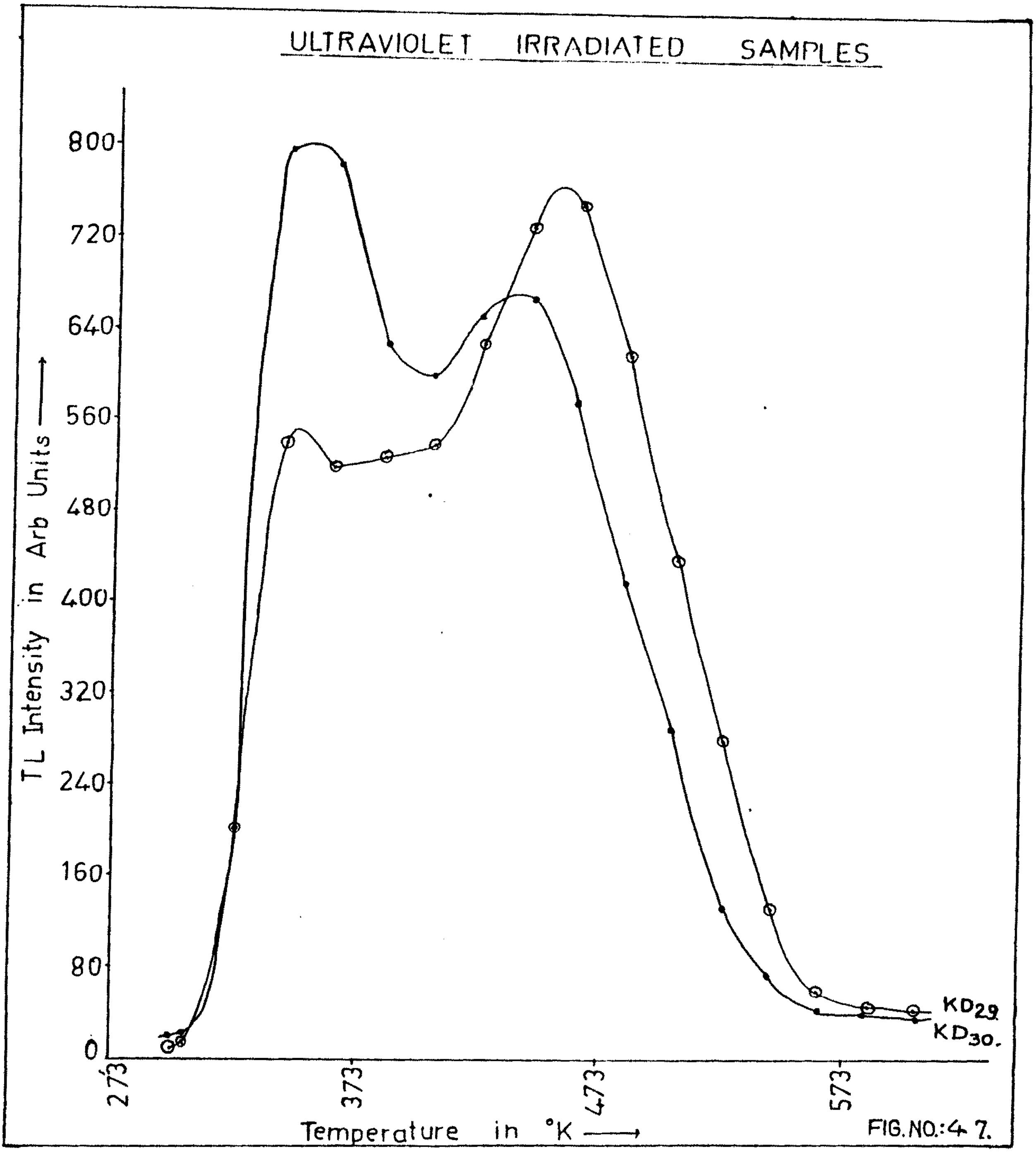

ULTRAVIOLET IRRADIATED SAMPLES
TL Intensity in Arb Units
0
80
160
240
320
400
480
560
640
720
800
273
373
473
573
Temperature in °K
KD29
KD30.

FIG. NO.: 4 7.

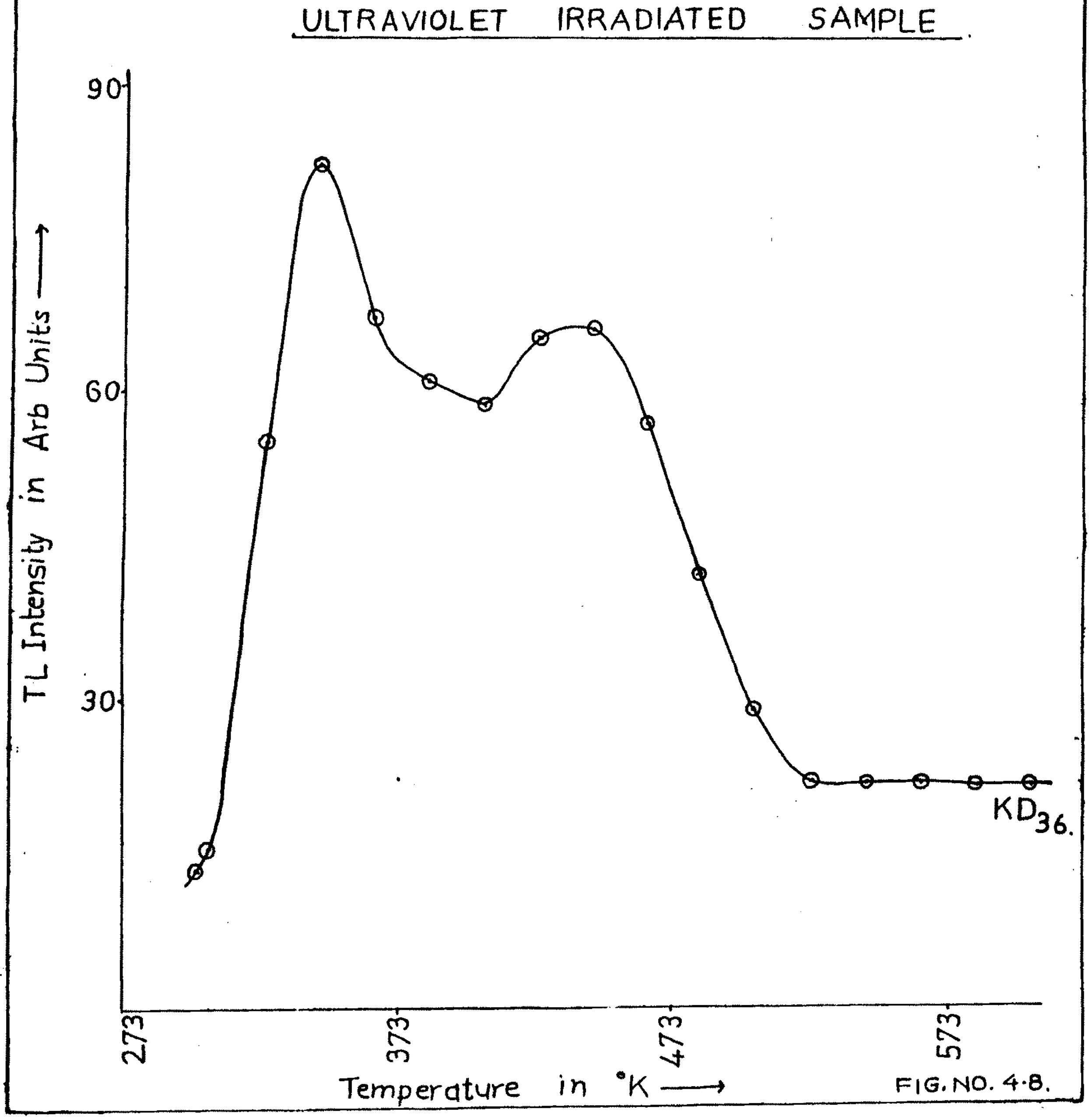

ULTRAVIOLET IRRADIATED SAMPLE
90
60
30
TL Intensity in Arb Units
273
373
473
573
Temperature in °K
KD36.

FIG. NO. 4·8.

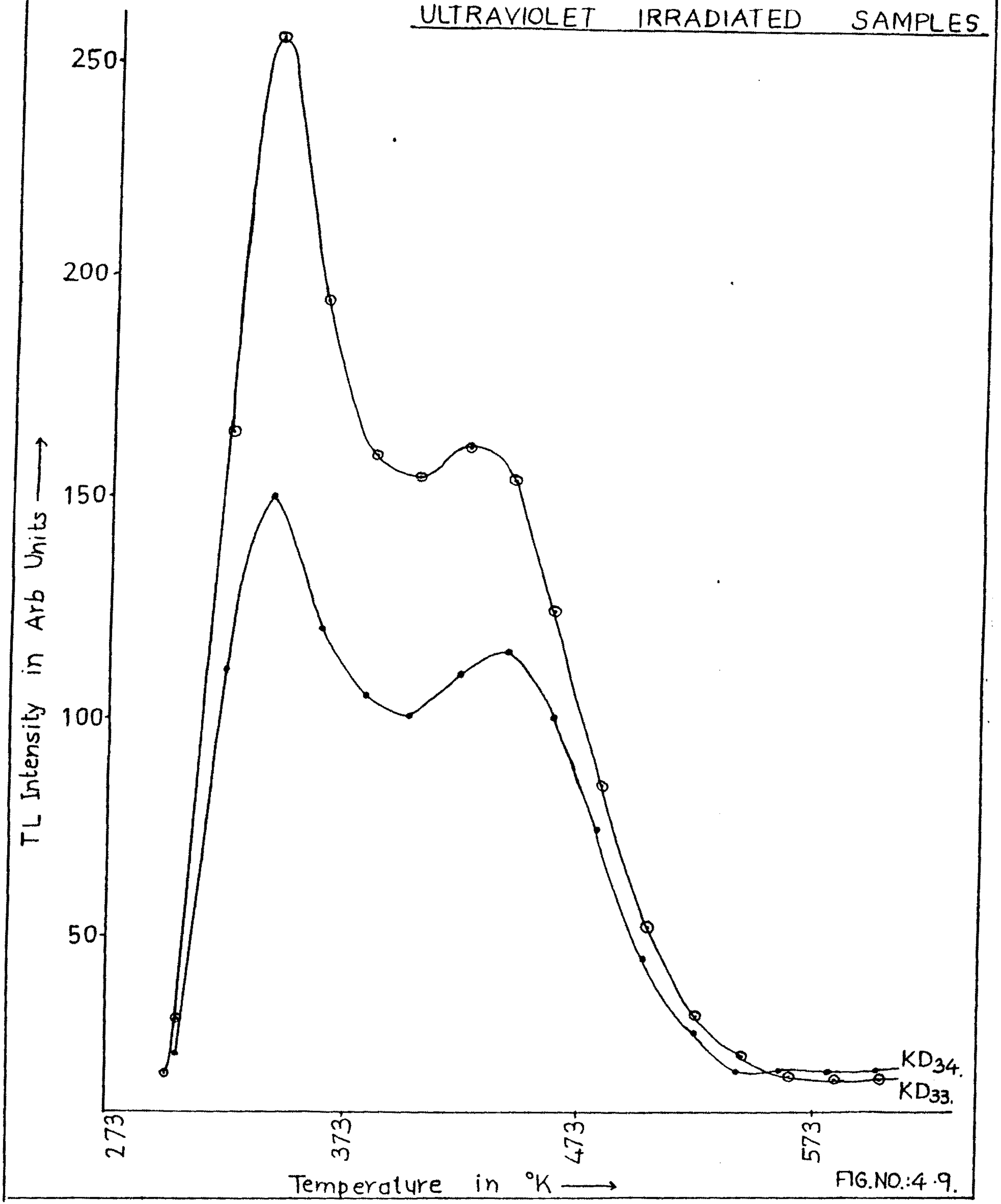

ULTRAVIOLET IRRADIATED SAMPLES
TL Intensity in Arb Units ⟶
250
200
150
100
50
273
373
473
573
Temperature in °K ⟶
KD34.
KD33.

FIG.NO.:4·9.

ULTRAVIOLET EXCITED SAMPLE.

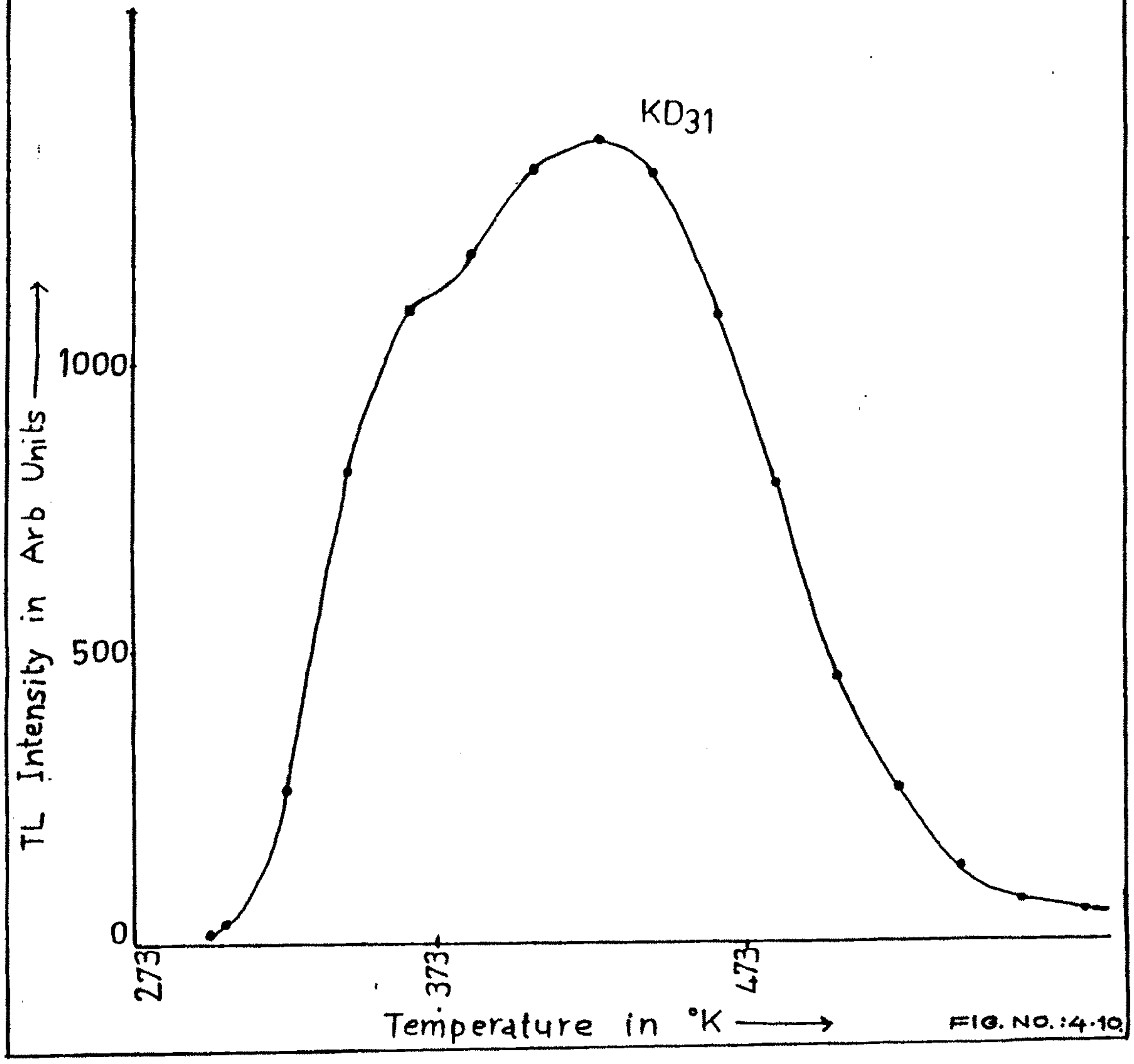


FIG. NO.:4.10

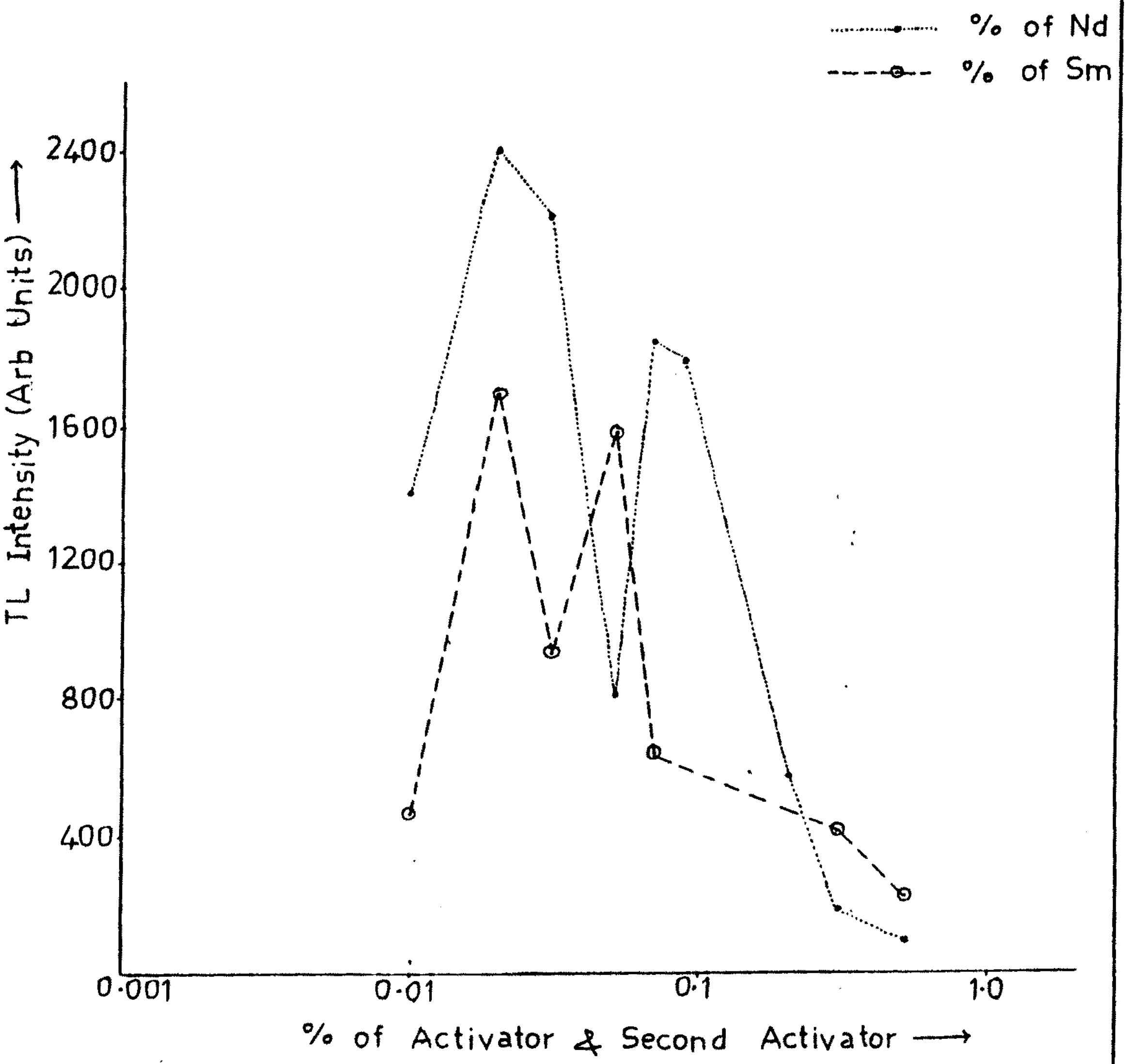
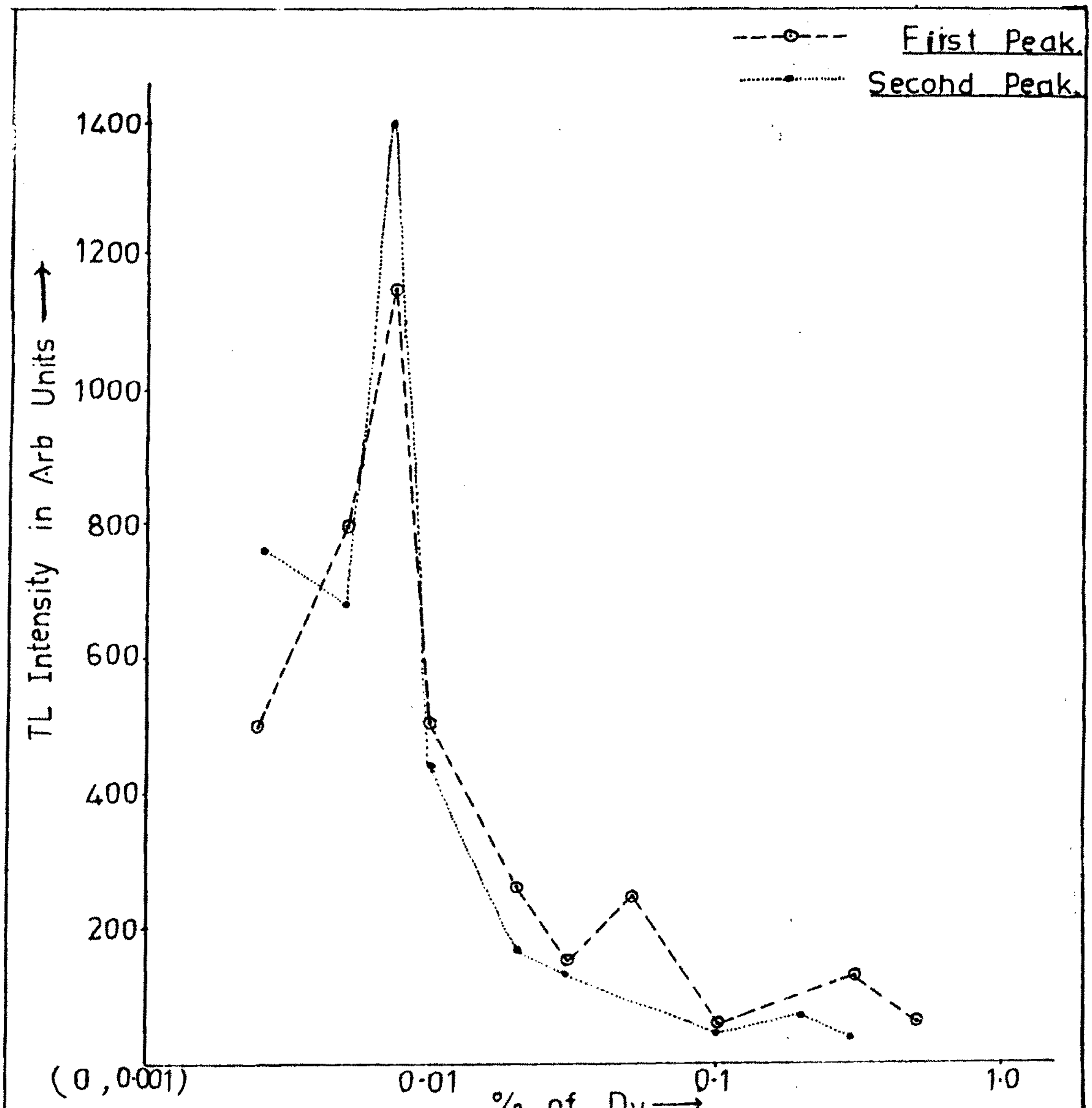

% of Nd
% of Sm
TL Intensity (Arb Units) ⟶
2400
2000
1600
1200
800
400
0·001
0·01
0·1
1·0
% of Activator & Second Activator ⟶

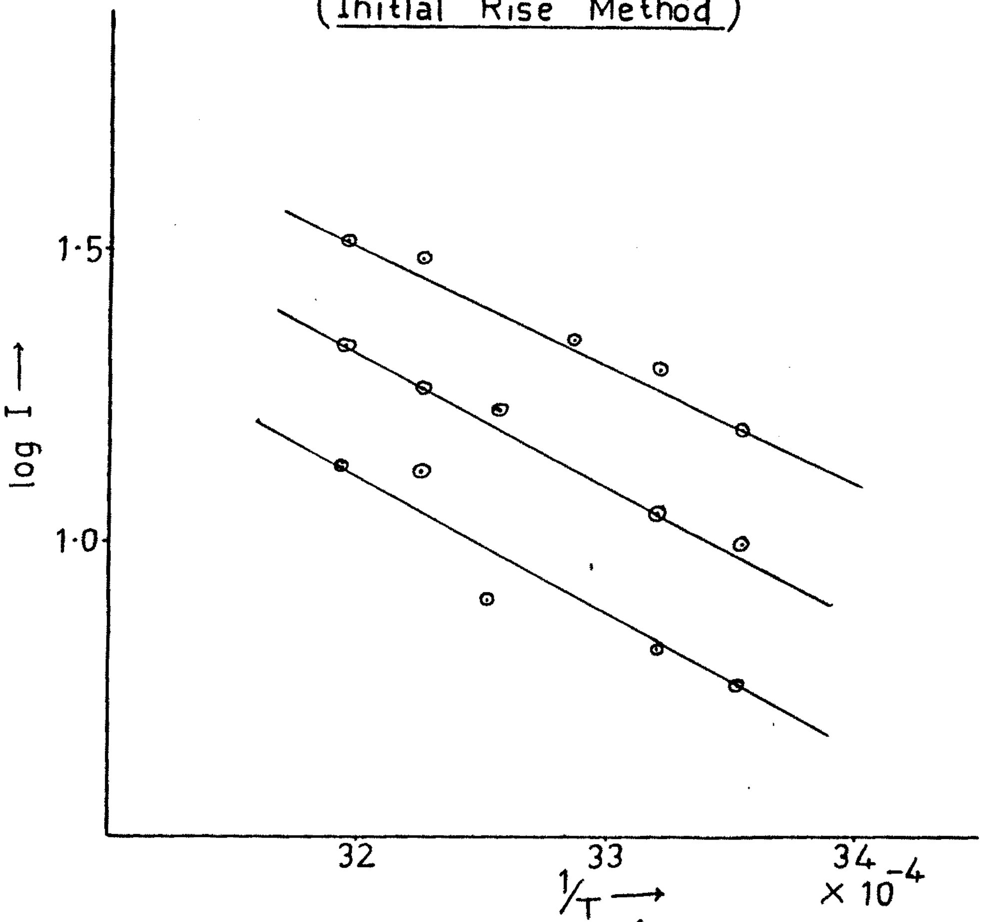
FIG. NO.: 4·11



Plot of TL Peak Intensity Vs % of Dy

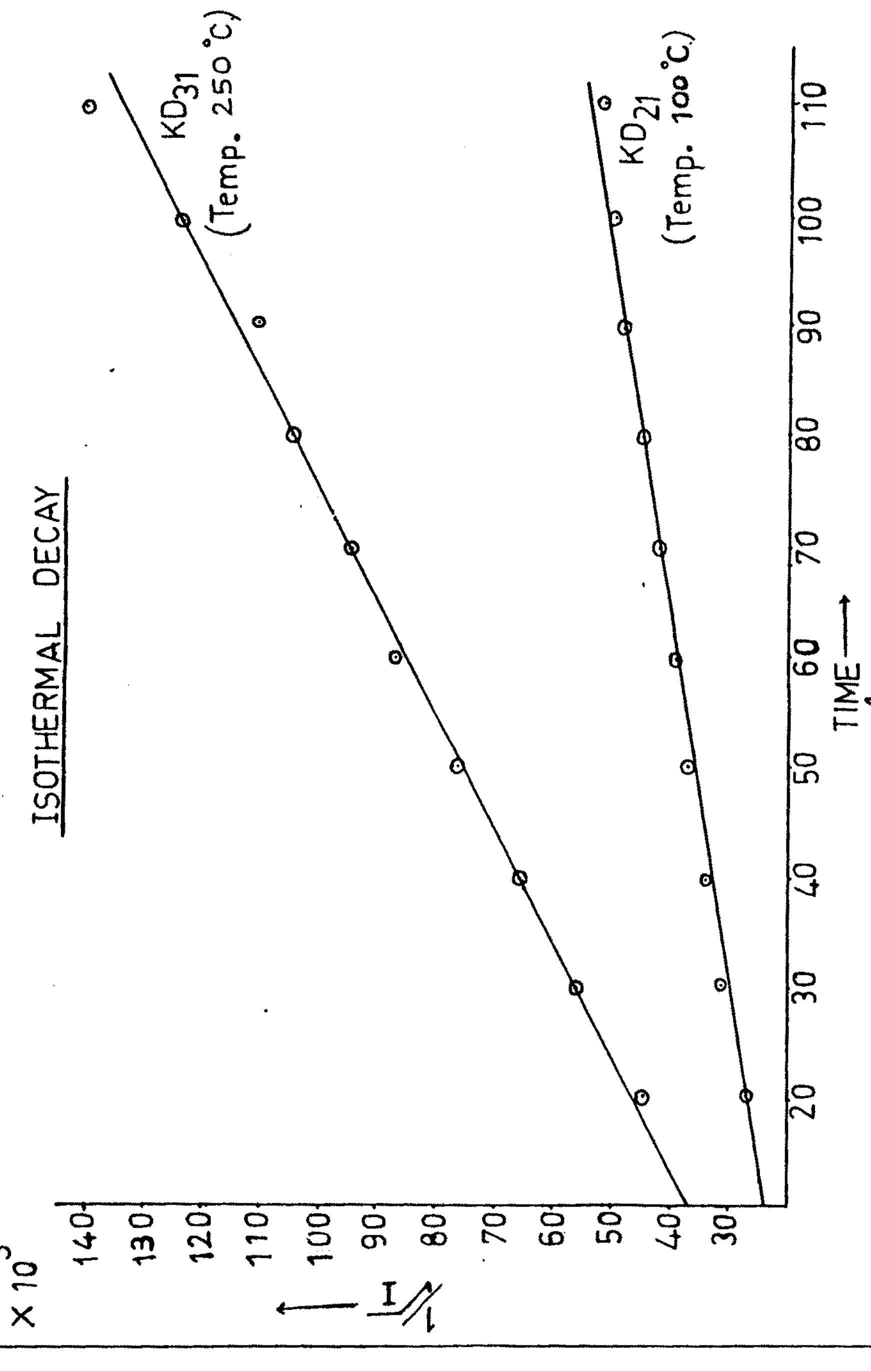
FIG. NO.: 4·12.

AREHENIUS PLOTS
(Initial Rise Method)



Plot of I Vs $\frac{1}{T}$ for Sample KD_{31}

FIG. NO.: 4·13.



Plots of $\frac{1}{\sqrt{I}}$ Vs Time

FIG. NO: 4·14

TL GLOW CURVES OF PHOSPHORS FOR DIFFERENT TIME OF EXCITATION

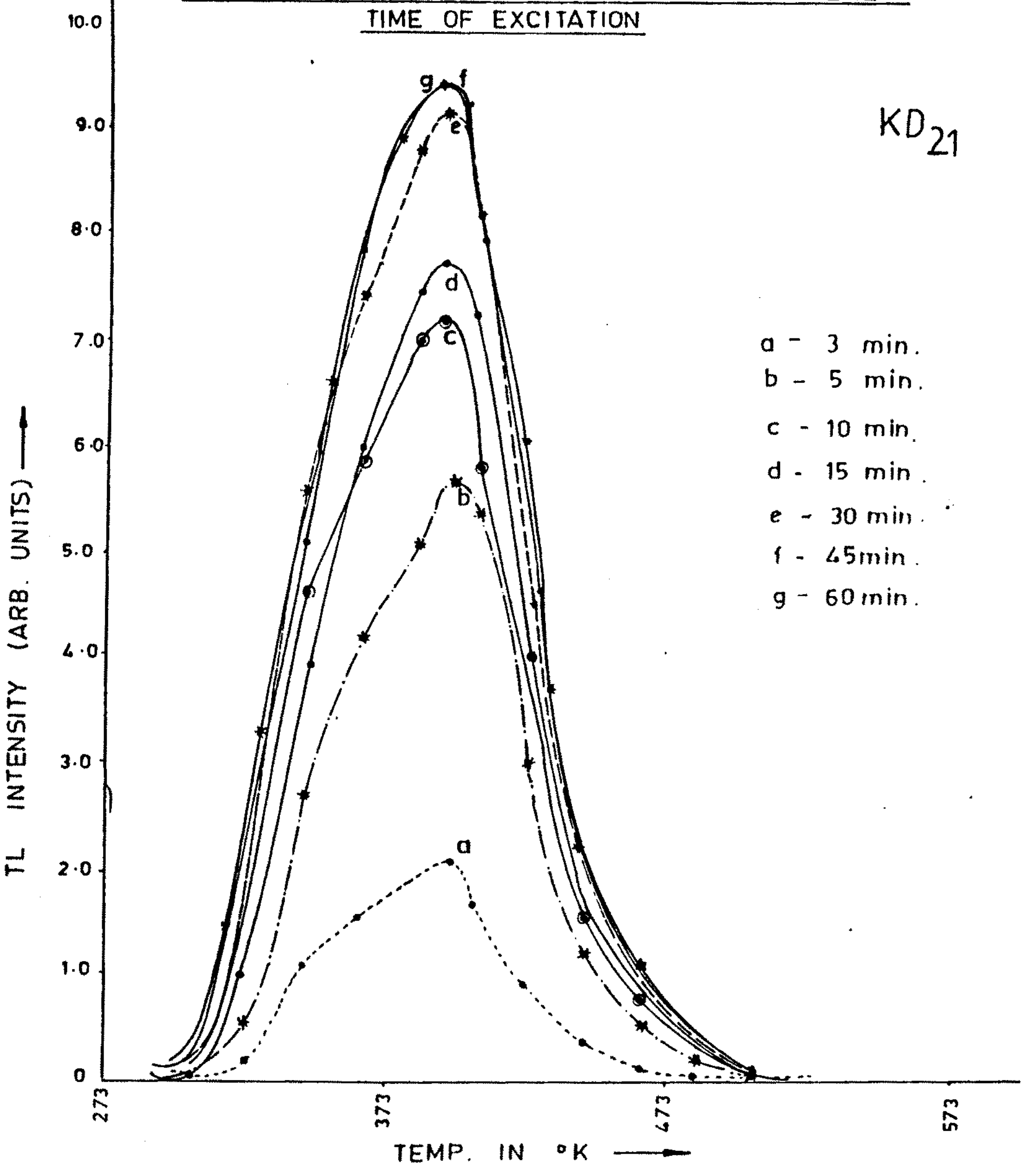


FIG. NO.– 4·15.

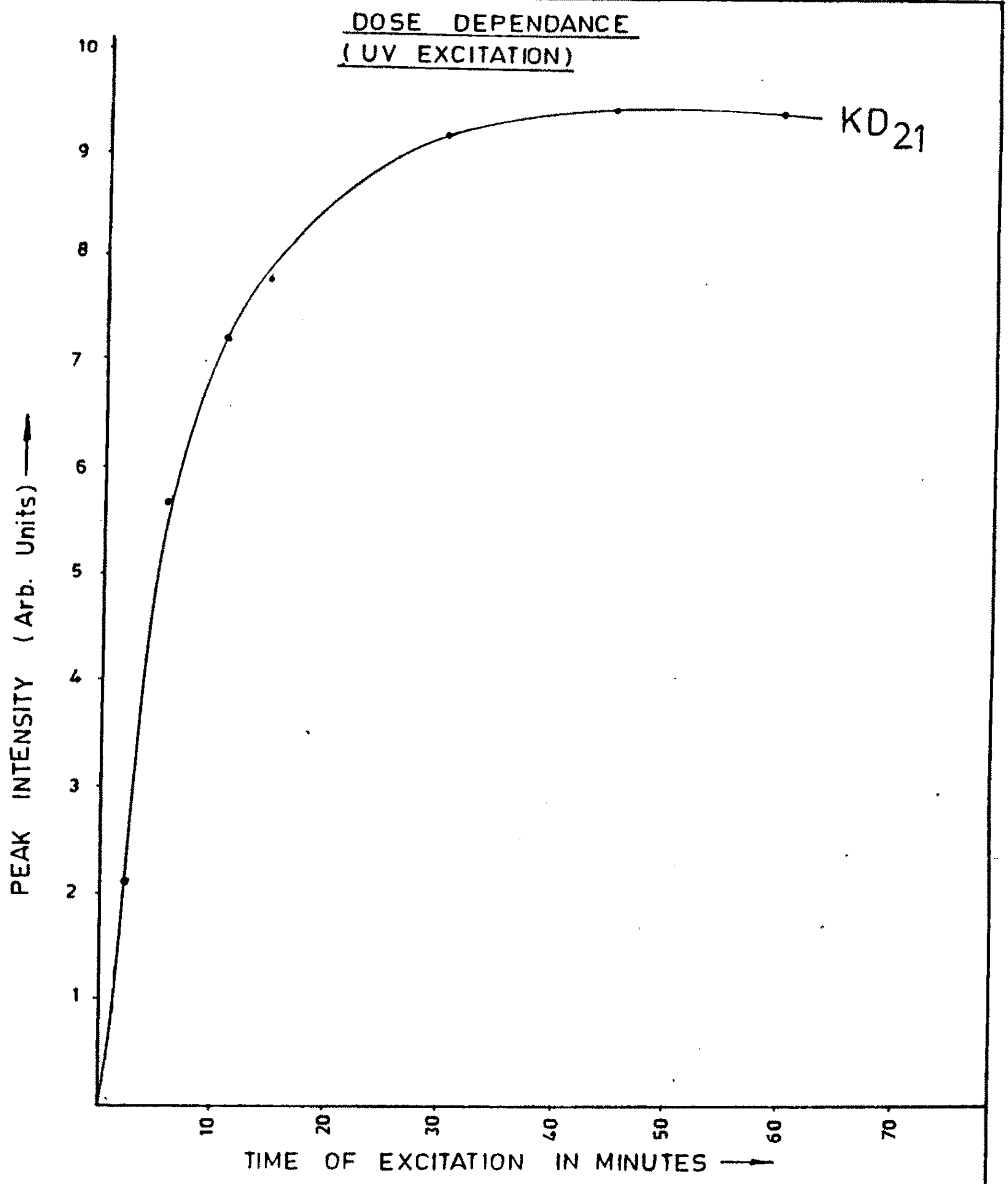

DOSE DEPENDANCE
(UV EXCITATION)
KD21
PEAK INTENSITY (Arb. Units)
10
9
8
7
6
5
4
3
2
1
10
20
30
40
50
60
70
TIME OF EXCITATION IN MINUTES

FIG. NO.- 4·16.

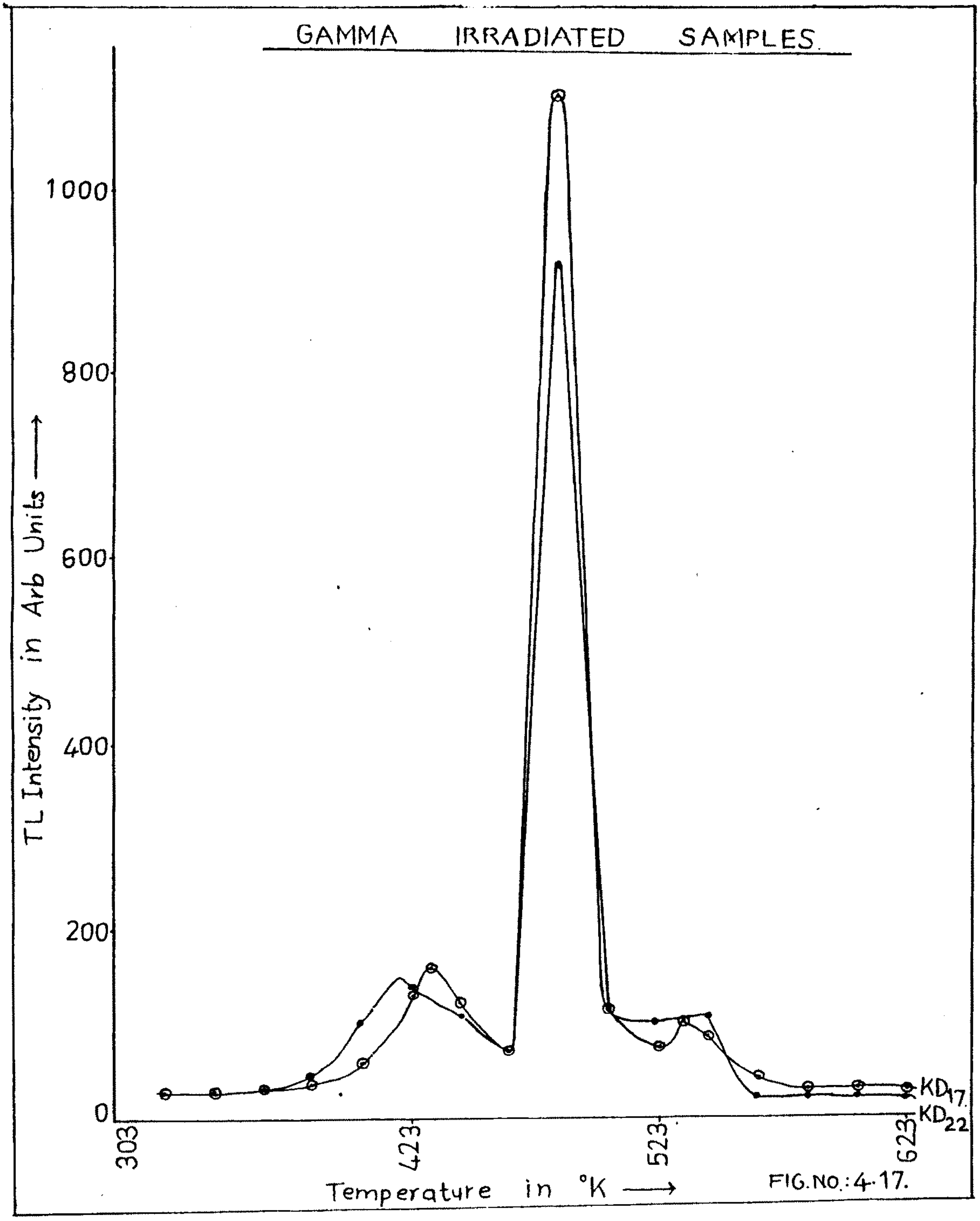

GAMMA IRRADIATED SAMPLES
TL Intensity in Arb Units ⟶
1000
800
600
400
200
0
303
423
523
623
Temperature in °K ⟶
KD17
KD22

FIG.NO.: 4·17.

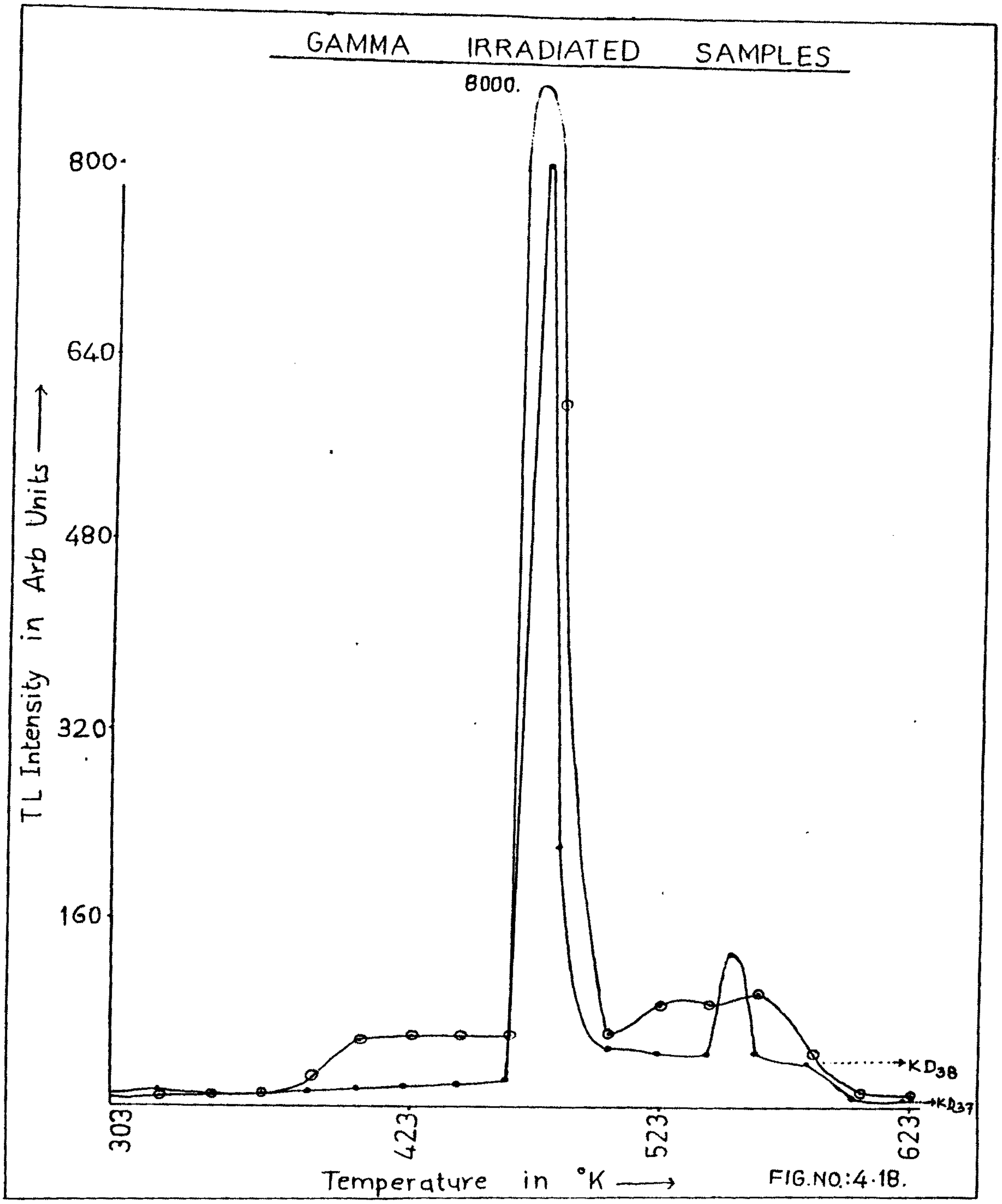

GAMMA IRRADIATED SAMPLES

FIG.NO:4·18.

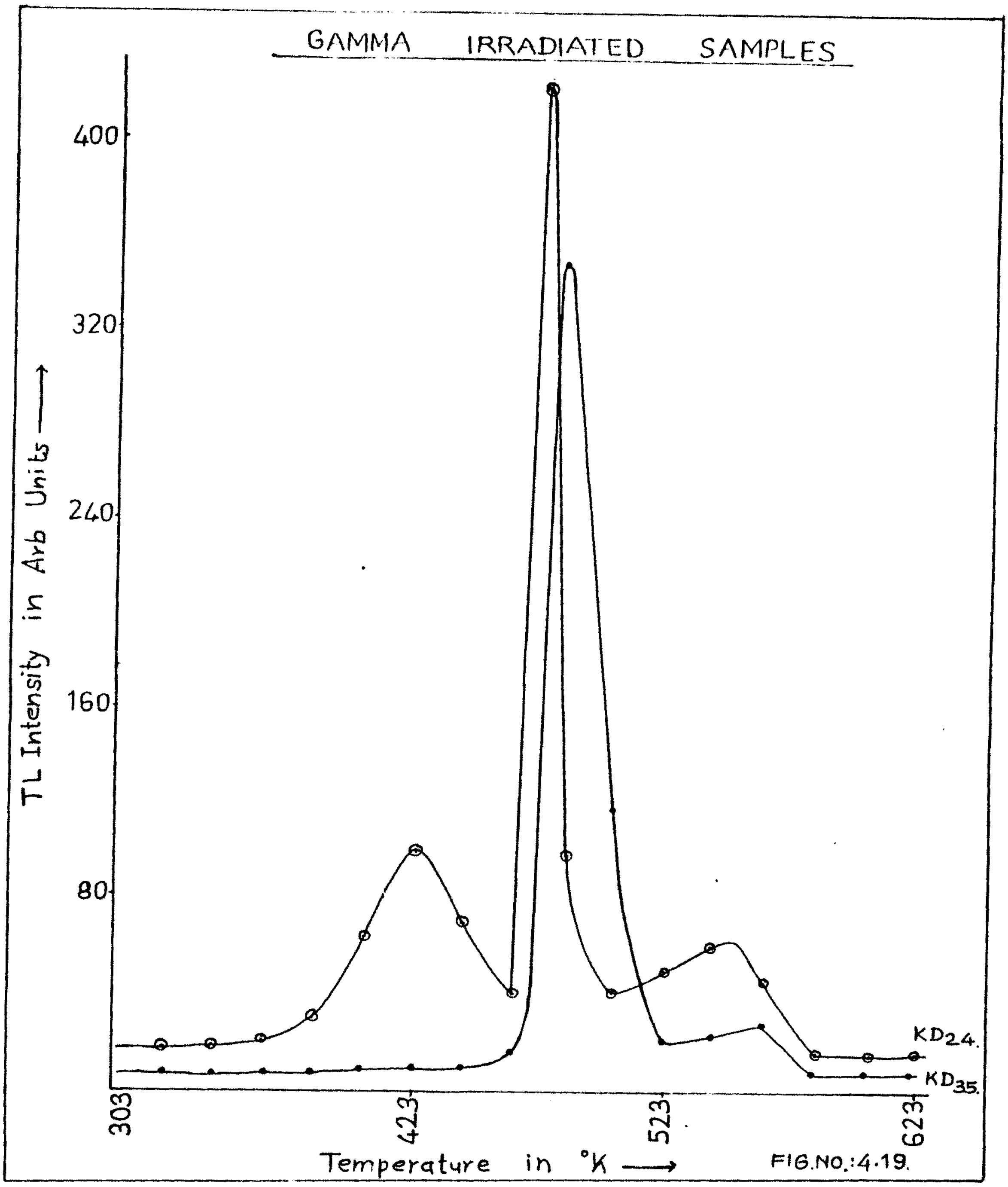

GAMMA IRRADIATED SAMPLES
TL Intensity in Arb Units ⟶
400
320
240
160
80
303
423
523
623
Temperature in °K ⟶
KD2.4.
KD35.

FIG.NO.:4.19.