# CHAPTER III

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## PHOTOLUMINESCENCE

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#### 3.1 INTRODUCTION

Photoluminescence is that phenomenon in which material absorbs light energy and re-emitts the energy in the form of visible light. In this process the absorbed energy is stored due to traps [electron or hole traps] developed in the phosphor during its preparation.

When the Phosphor is prepared, certain localized energy levels (traps) are created in it. Electrons (or holes) get trapped in it, when energy is supplied to these trapped electrons (or holes) in the form of incident light radiation, like ultra violet, gamma<sup>°</sup> radiation, they get detrapped and there is an emission of light. Detrapping (luminescent output) reduces with time. Thus the phosphorescence decay is observed i.e. light output versus time curve is observed, when the source of excitation is removed.

The analysis of phosphorescence decay curves furnishes some useful insight into the basic mechanism involved in the process. The study of phosphorescnece decay provides information about nature of trapping states, energy levels of luminescent material and the type of kinetics involved in the luminescence process.

In the present investigations  $CaSO_{4}$  doped with Mn and rareearths specially Eu (as revealed from TL analysis) is studied to get the information about the following aspects.

1] Nature of decay law.

2] Energy distribution of traps.

3] Kinetics involved in the decay mechanism.

4] The effect of activators on the decay behaviour.

#### 3.2 THEORETICAL BACKGROUND

In 1935 Jablonskii<sup>(1)</sup> made an important step in the theory of Phosphorescence and that was for the decay of emission from organic molecules in rigid media. He proposed an energy level scheme for emitting centre as shown in fig.(1.4). The fluorescence is given by, the transition between the excited state F and the ground state G', but excited molecules or centres may relax to the metastable state M', transitions  $M \rightarrow G$  being forbidden. To return to ground state the transition  $M \rightarrow F$  must be effected by thermal or optical activation. Thus phosphorescence emission due to  $F \rightarrow G$  is conditioned in rate by optical process  $M \rightarrow F$ . If the energy required for the latter is E', then the probability per second that it occurs is given by

 $P = Se^{(-E/KT)}$  .. (3.1)

where 'T' is the absolute temperature of the phosphor, 'S' is the escape frequency factor and 'E' is the electron trap depth.

In general, a phosphor contains more than a single trap and phosphorescnece is known to be cumulative effect of traps of different depths. Its intensity is dependent on the rate of escape of electrons from traps. The retrapping of electrons in traps also affects the behaviour of phosphorescence.

#### 3.2.1 DECAY LAWS

The phosphorescence decay may be either exponential or hyperbolic <sup>(2)</sup> depending upon the type of kinetics involved in the

#### luminescnece process.

1) Exponential decay

In this, as the name suggests, the emission intensity diminishes exponentially with time. The finite delay in emission of absorbed energy is due to life time of excited state of the emitting atom, ion or molecule. If 'p' is the transition probability for return of the centre to the ground state and 'n' centres are excited at any instant, then

$$\frac{dn}{dt} = J - pn \qquad .. \qquad (3.2)$$

where 'J' is the number of excited centres per second by the incident radiation. The transition probability 'p', according to Randall and Wilkins <sup>(3)</sup> is given by equation (3.1) viz.  $p = S-e^{(-E/KT)}$ .

The decay of luminescence is given by equation (3.2) with J=0. The equation (3.2) then becomes -

$$\frac{dn}{dt} = -pn$$

 $\frac{1}{n} = -pdt$ 

On integration above equation becomes,

$$n = n e^{(-pt)}$$
 .. (3.3)

where  $n_0^{\prime}$  is the number of excited electrons at t = o, the time when excitation ceases.

The luminescnece intensity is given by,

$$I = \frac{-dn}{dt} = -(-pn)$$
  
= P.n<sub>o</sub>.e<sup>(-pt)</sup>  
. I = I<sub>o</sub>e<sup>(-pt)</sup> .. (3.4)

Where I<sub>0</sub> is the intensity at t = 0 and p =  $\frac{1}{\gamma}$  being life Time of excited state.

The equation (3.4) shows that, decay is exponential and the rate of decay depends only upon the transition probability 'p'. The exponential decay occurs when the kinetics of luminescence process is of the first order i.e. when electron traps are situated quite close to the luminescnece centres. The equation (3.4) is useful in evaluating the trap depth.

2) Hyperbolic decay

When the luminescnece process is of the second order, this type of decay results i.e. when electron traps are locted away from luminescence centres.

Let there be 'n' impurity centres, with which only n number of electrons combine at a time. If 'p' is the probability with which an electron combines with any of the centres in time 'dt', then,

 $p = Andt \qquad \dots \qquad (3.5)$ 

where A is a constant known as recombination coefficient.

If all the electrons return to the ground state at the centres. through the conduction band with the above said probability 'p' then the rate of decay will be,

On integration,

 $n = \frac{n_o}{1 + n_o At}$  ... (3.7)

And the luminescence intensity is given by

$$I = -\frac{d_{11}}{dt} = -(-An^{2})$$

$$= \frac{n_{0}^{2}}{(1+\gamma_{0}At)^{2}}$$

$$= \frac{I_{0}}{(1+\sqrt{t})^{2}} \dots (3.8)$$

where  $d_{n_0} = n_0^{n_0} A$  is another constant

For large values of t,  $(t \gg 1)$  the equation (3.8) can be written as,

$$I = \frac{I_0}{(q_t)^2}$$
 ... (3.9)

Treating more generally in the light of different capture cross sections for electrons empty centres and traps,  $Adirowitch^{(4, 5)}$  arrived at an approximate Becquerel type relation of the form,

$$I = \frac{Constant}{(t + to)^b} \qquad .. \qquad (3.10)$$

where 'b' depends on the ratio of capture cross-section of traps to that of empty centres. However, this equation fails in cases where well separated groups of traps exist.

# 3.2.2 EFFECT OF STEADY EXCITATION OF A PHOSPHOR ON THE FILLING OF ELECTRON TRAPS

Luminescnece intensity of a phosphor reaches to a constant value if it is excited at fixed temperature by steady excitation <sup>c</sup> source. This state of phosphor is called equilibrium state, and in this condition, the concentration of filled electron traps is in equilibrium. Depending on the relative location and distribution of traps the following cases arise. A) When traps are located close to the luminescence centres (First order kinetics).

Let 'J' be the intensity of excitation. Then the rate of electron raising to the excited state is proportional to 'J' and is given by CJ. Where 'C' is constant of proportionality. If there are 'n'number of electrons in the 'N' traps, then the rate of capture of excited electrons in traps is CJa(N-n), 'a' being the probability of capture per trap. The rate of escape of electrons from traps is given by  $ns \cdot e^{(-E/KT)}$ . Under equilibrium condition, the rate of capture of excited electrons in traps and the rate of electrons escaping from traps will be equal, and thus,

$$CJ_{n}(N - n) = ns \cdot e^{(-E/KT)}$$
 (3.11)

from which we get,

n = 
$$\frac{N}{\frac{1 + Se^{(-E/KT)}}{A}}$$
 ... (3.12)

Where  $A = CJ_{a}$  is a factor directly proportional to the intensity of excitation.

B) When traps are located away from the luminescence centres (Second Order kinetics)

1 m 1

Let 'n' be the number of trapped electrons and the number of these in conduction band. The (m+n) is the number of empty luminescence centres and rate of electrons returning from the conduction band is given by,

 $\frac{dm}{dt} = 0 = CJ - \beta m (m+n) + nse^{(-E/KT)} - mb (N-m) ... (3.13)$ and the rate of electrons returning from the conduction band is given by,  $\frac{dn}{dt} = 0 = nse^{(-E/KT)} - mb (N - n) .. (3.14)$ where '\b' and 'b' are constants and 'CJ' is the rate of electrons raising to the excited state.

If the excitation is not of an appreciably low intensity, the number of electrons in the conduction band is much greater than the number of trapped ones and thus (m+n)

Hence  $\beta m^2 = CJ$  ... (3.15) and there fore

$$n = \frac{N}{\frac{1 + se^{(-E/KT)}}{B}}$$
 ... (3.16)

where  $B = b \sqrt{CJ/\beta}$  and thus is proportional to the square root  $\sim$  of the excitatin intensity.

#### C) When the traps exist with complex distribution (General order or intermidate kinetics) :

If the form of specific distribution of traps is known, the derivations of equations (3.12) and (3.16) can be extended further to over complex trap distribution. In most practical cases, the number of traps 'N' of different trap depths does not vary rapidly with 'E' over most of the range of E values. Thus if 'N' is assumed to be constant or slowly varying, the total number of filled traps from a given excitation intensity can be obtained. Let this number be  $n_{T}$ , then in most cases,

$$n_{T} = \int_{0}^{E} \max.$$
Using the equation (3.12) we get
$$n_{T} = \int_{0}^{E} \frac{N}{1 + \frac{Se^{(-E/KT)}}{A}} \cdots$$
(3.18)

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For all practical excitation intensities  $A \ll 5$  and thus equation (3.18) yields on integration.

 $n_T = NKT \log (A' + 1)$  .. (3.19) where  $A' = As^{-1} e^{(-Emax/KT)}$ , is proportional to the excitation intensity.

At high excitation intensities, when  $A' \ge 1$ , the number of filled traps will be a linear function of logarithm of the excitation intensities provided that A << S. When 'A' approaches' S', a saturation state will be reached A similar logarithmic relation can be obtained by using equation (3.16) which induces consideration of retrapping.

#### 3.2.3 PHOSPHORESCNECE DECAY FOR DIFFERENT TRAP DISTRIBUTIONS.

(Considering retrapping negligible)

In general, a phosphor contains traps of various depths. If there are 'N' number of traps with activation energies lying between E and E + dE, then assuming retrapping to be negligible, the phosphorescence intensity 'I' at time 't' after cessation of excitation is given as follows :

$$I = \int_{E \text{ min.}}^{E \text{ max.}} Ns \cdot e^{-E/KT} \cdot e^{[-st} e^{-E/KT]} dE \dots (3.20)$$
  
=  $\frac{Ns}{e^{(s.t.)}} \int_{E \text{ min.}}^{E \text{ max.}} e^{(-E/KT)} e^{[e^{(-E/KT)}]} dE \dots (3.21)$ 

Considering N to be constant over an energy range of 0 to infinity, the following three cases of interest arise according to the distribution considered.

#### A) Uniform Trap Distribution.

The distribution of traps is said to be uniform, if a phosphor contains an equal number of traps of all depth in the range of energy from zero to infinity. Then integration of equation (3.21) gives -

$I = \frac{NKT}{t} (1 - e^{-s \cdot t})$	••	(3.22)
If $St \gamma \gamma 1$ , then		
$I = \frac{NKT}{t}$ = NKT t <sup>-1</sup>	••	(3.23)
= $Constant t^{-1}$	••	(3.24)

Thus the Phosphorescence intensity (1) is inversely proportional to decay time (t) and a plot of I versus t  $^{-1}$  should be a straight line. Moreover, plot of log I against log t should be a straight line with a slope equal to -1

B) Quasi-Uniform Trap Distribution.

The phosphors having number of traps 'N' which do not vary too rapidly with values of 'E' in a complete distribution are said to possess quasi uniform trap distribution. Here the intensity of phosphorescnece decay at any time t' is proportional to the number of electrons in traps of mean life time  $\gamma$  given by,

 $\gamma = s^{-1}$ ,  $e^{(E/KT)}$ . From equation (3.23) the product '1.t' is found to be proportional to 'E'. Thus a plot of the product '1.t' against log t for a given phosphorescnece decay will represent the variation of 'N' with 't' and gives an approximate idea of the trap distribution.

C) Exponential Trap Distribution.

If we have  $N \sim e^{(-\beta - E)}$  as is found in some experimental cases, then for st >> 1, we have,

 $I = constant t^{-(\beta KT + 1)}$  ... (3.25)

i.e. power of 't' varies linearly with the phosphor temperature, the constant ' $\beta$ ' (always positive) can be found experimentally and approximately from the shape of thermoluminescnece curve.<sup>(3)</sup>

When  $\beta KT = 1$  the equation (3.25) is correlated with the bimolecular law and when  $\beta KT = 0$ , the case becomes of uniform Trap distribution i.e. reciprocal law holds good. At room-temperature many phosphors show the decay of the type given by equation (3.25). With any trap distribution covering a wide range the decay is influenced slightly by variation of temperature because, with rising temperature deeper traps supply electrons at the same rate at which shallow traps supply electrons at a lower temperature. At constant temperature, on the other hand, at time 't' most of the light emission by a phosphor with continuous trap distribution is due to traps in which the electrons will have the mean life time  $\gamma = t$ 

### 3.2.4 RETRAPPING OF ELECTRONS DURING PHOSPHORESCENCE

It is obvious that, the escaping electrons from trap will always have a finite probability of being trapped before recombination with luminescence centres. The process of retrapping causes marked changes in phosphorescence characteristics <sup>(6)</sup>

Garlick<sup>(7)</sup>, considering the effect of retrapping in monomolecular case, obtained an expression for the intensity -

$$I = \frac{n_{o}^{2} \cdot e^{(-E/KT)}}{N [1 + \frac{n_{o}}{N} \text{ st } e^{(-E/KT)^{2}}]} \cdot (3.26)$$

where N' is the total number of traps and no' is the number of empty centres or filled traps initially. The equation can be further simplified. Considering the case  $n_0 = N$ , i.e. traps are saturated at the commencement of decay. This results in

$$I = \frac{NS \cdot e^{(-E/KT)}}{[1 + st \cdot e^{(-E/KT)^2}]} .. (3.27)$$

At long decay times  $(t \gg 1)$  the equation (3.26) becomes,

$$I = \frac{N e^{(-E/RT)}}{st^2} ... (3.26)$$

Thus, for the traps of one depth only, retrapping process causes a fundamental change in the form of decay from exponential to hyperbolic  $\binom{8}{1}$ . A more general treatment of phosphorescence due to traps when retrapping occurs has recently been given by Klasens and Wise  $\binom{9}{1}$ .

#### 3.3 RESULTS AND DISCUSSION

#### 3.3.1 DECAY CURVES

Figures 3.1 to 3.3 show typical decay curves obtained for various samples of  $CaSO_{44}$  doped with Mn and Eu of different concentrations. From decay curves it is observed that, initially intensity decreases very fast with time and then decreases considerably at very slow rate. The decay curves appear to be of the same general nature as reported for alkaline earth sulphide and sulphate phosphors (10-14,25,26).

The first step in the analysis of decay curves is to decide the mode of decay i.e. exponential, hyperbolic or power law decay. To examine the possibility of simple exponential decay with single trap depth as given by eq. (3.4) graphs of logi versus logt are plotted. The plots are found to be non-linear, indicating that decay lowever, plots of log 1 vs log t are linear is not exponential. Typical plots are shown in the fig. (3.4, 3.5). This indicates that decay may be hyperbolic or power law.

> Thus, the observed decay can be represented by the equation.  $I = I_0 t^{-b}$  ... (3.29)

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where I is the intensity at time 't',  $I'_0$  is the maximum intensity. of the decay at the start and 'b' is the decay constant.

#### 3.3.2 CORRELATION COEFFICIENT

The degree of linearity between log versus logt is confirmed by evaluating the correlatin coefficient(r) using the equation

$$r = \frac{N\Sigma x y - \Sigma x \Sigma y}{[N\Sigma x^{2} - (\Sigma x)^{2}]^{\frac{1}{2}} \cdot [N\Sigma y^{2} - (\Sigma y)^{2}]^{\frac{1}{2}}} \quad .. \quad (3.30)$$

where  $x = \log t$  and  $y = \log t$  and N is the number of observations. The magnitude of 'r' signifies the closeness of relationship while its sign indictes whether y increases or decreases with x, then the relation is linear, the value of r' is equal to unity.

In the present study, values of 'r' for different samples are shown in table (3.1). The values of 'r' for some sample are nearly equal to -1. This indicates that relation between log1 versus logt is close to linear. The negative sign of 'r' indicates that intensity decreases with time.

#### 3.3.3 DECAY CONSTANT

The value of decay constant indicates the rate of decay. Higher the value of decay constant (b), faster is the decay rate and vice versa. The value of 'b' also provides information about relative popultion of traps at various depths.

The value of decay constant is calculated from the formula of least squares<sup>(15)</sup>using the relation

$$b = \frac{N\Sigma xy - \Sigma x\Sigma y}{N\Sigma x^2 - (\Sigma x)^2} \qquad (3.31)$$

where  $x = \log t$ ,  $y = \log t$ , N is equal to number of observations. The values of b calculated using above eq.(3.31) are shown in the table 3.1. Values of 'b' obtained from slopes of logi versus logi

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plots are also given in the same table. Calculated values of b using eq.(3.13) and those from graphs nearly agree with each other.

#### 3.3.4 VARIATION OF DECAY CONSTANT FOR DIFFERENT PHOSPHORS

The variation of decay constant for different phosphors is as shown in the figure (fig.3.10). From this figure it is clear that, for different concentrations of impurities, decay constant varies slightly in the range of 0.3 to 0.6 hence assumed practically constant. This indicates that, a single group of traps at one depth contributes to the phosphorescence decay<sup>(14)</sup>. This also indictes that, activators probably do not create new traps but, modify the relative importance of traps contributing to the phosphorescence decay.

#### 3.3.5 "PEELING OFF" DECAY CURVES

In the present investigation, the phosphorescence decay can be represented as

 $I = I_0 t^{-b}$ 

For hyperbolic decay, 'b' should be equal to 2 and for power law decay it should be equal to 1. The value of b is neither exactly 2 nor exactly 1. It is nearly equal to 1. Thus the possibility of hyperbolic decay can be eliminted and the resulting decay may be power law decay resulting from traps of similar origin.

However, the observed power law decay can be explained on the basis of monomolecular superposition theory suggested by Randa-II and Wilkins<sup>(3)</sup> and followed by other workers <sup>(14,16,17,18)</sup>. Such decay results due to the superposition of various exponentials, corresponding to different traps and is expressed by the equation -

where  $\begin{bmatrix} 1 & 1 & 1 & 1 \\ 0 & 1 & 2 & 0 \\ n & 1 & 2 & 1 \end{bmatrix}$  are the starting contributions to luminescence intensity by first, second ....n<sup>th</sup> exponential component and

$$P_{1} = Se^{-E_{1}/KT}$$

$$P_{2} = Se^{-E_{2}/KT}$$

$$P_{n} = Se^{-E_{n}/KT}$$

are the transition probabilities of an electron escaping from traps of the depth  $E_1$ ,  $E_2$ , ...,  $E_n$  respectively.

Each decay curve can be split into a set of exponentials by the method suggested by  $Bube^{(19)}$  and followed by others  $^{(14,16,18)}$ .

In present investigations all the decay curves are split into exponentials (fig. 3.6 to 3.9). The activation energies corresponding to these exponentials are calculated. The slopes  $P_1, P_2, P_3$  of straight lines (tangent to the curve) of log I x t graphs plotted on semi log paper are calculated. The values of 'E' thus evaluated for slowest, middle, and fastest exponentials are shown in the table 3.2. The value of 'S' used in this calculation is taken from thermoluminescence studies of the same samples.[chapter IV, Table No.4, 1].The value of 'E' lies in the range of 0.4 to 0.6 eV. These values are in agreement with that of previous workers.<sup>(14,26,27)</sup>

#### 3-3.6 EFFECT OF ACTIVATOR CONCENTRATION ON TRAP DEPTHS

The trap depth values are given in the table 3.2. From this table it is observed that, there is no significant change in trap depth with activator concentration. This suggests that, the activators do not introduce any new traps. The relatively small and unsystematic variation observed in different samples maybe due to perturbation of trapping states (20, 21). Further, there is no systematic change in

activation energies for the phosphors with changing concentration of the activators.

The trap depths are seen to have lower range than those calculated from thermoluminescence studies for the same sample. This may be due to the emptying of the shallow traps at room temperature at which PL is recorded

#### 3.3.7 DISTRIBUTION OF TRAPS

The distribution of traps may be uniform, quasi uniform or exponential  $\binom{22}{}$ . For uniform trap distribution over a wide range, the relation between phosphorescence intensity and time for st  $\rangle$  1 is given by -

 $I = I_0 t^{-1}$  ... (3.33) This relation is similar to  $I = I_0 t^{-b}$ . Thus for uniform trap distribution b' should be equal to unity over a wide range.

Observed values and calculated values of 'b' show a considerable departure from unity  ${}^{(14)}$  (less than unity). On the other hand straight line nature of graph log I versus log t is suggestive of uniform distribution  ${}^{(27, 28)}$ . This indicates that trap distribution is non uniform, more probably quasiuniform as revealed from values of 'b'. Further investigations are needed to confirm exact nature of trap distribution.

### 3.3.8 KINETICS OF LUMINESCENCE

The kinetics involved in the decay process may be of the first order (monomolecular), second order (bimolecular), or intermediate. For decay curves, resulting from traps of single depth, the monomolecular process involves the exponential decay. The bimolecular process involves the hyperbolic decay. For the processes that are neither of the first order nor second order (24) the power law holds good. For the first order kinetics the graph of log I vs. t plotted on semilog paper must be a straight line. In the present investigation it is not so. It indicates that kinetics is not of first ordeer.

Also for second order and intermediate order, the slope of the graph of log I vs log t has the values -2 and -1. In the present study, the slope of log I vs log t is not equal to -2 hence kinetics may not be second order.

However, the decay can be represented by a power law equation of the type  $I = I_0 \cdot t^{-b}$  but the value of b is not exactly as required by intermediate kinetics. On the other hand, the observed power law decay could be well explained on the basis of monomolecular superposition theory. This suggests that kinetics involved is likely to be monomolecular.

#### 3.4 SUMMARY

The results of PL study can be summarised as;

- 1] The nature of decay curve for various samples is similar and may be expressed by an equation  $I = I_{a} t^{-b}$
- 2) Nature of decay is of power law type in some cases and can be explained in terms of superposition of various exponentials of monomolecular type.
- 3] The value of decay constant is less than unity and the distribution of traps may be quasiuniform.
- 4] The trap depths of effective levels are relatively insensitive to the concentration of activators Mn and Eu.
- 5] The probable kinetics of decay process is likely to be monomolecular.

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# TABLE NO.3.1

Values of correlation coefficient and decay constant for  ${\rm CaSO}_4:{\rm Mn}:{\rm Eu}$  phosphor.

Sample No	Description	Correlation coefficient(r) (-ve)	Decay consta from calculation (-ve)	nt from Graph(-ve)
PD 15	CaSO 4: Mn 0.1: Eu 0.01	0.9834	0.5360	0.4632
PD 16	CaSO <sub>4</sub> :Mn <sub>0.1</sub> :Eu <sub>0.05</sub>	1.002	0.5148	0.4923
PD 19	CaSO <sub>4</sub> : Mn <sub>0.1</sub> : Eu <sub>1</sub>	0.9974	0.5554	0.4266
PD 4	CaSO <sub>4</sub> :Eu <sub>1</sub>	0.6366	0 <b>.3689</b>	0.4333
PD 12	CaSO <sub>4</sub> :Mn <sub>0.1</sub> :Eu <sub>0.1</sub>	0.9700	0.602	0.5833
PD 22	CaSO <sub>4</sub> : Mn <sub>0.3</sub> : Eu <sub>0.1</sub>	0.6629	0.4193	0.4
PD 23	CaSO <sub>4</sub> : Mn <sub>0.5</sub> : Eu <sub>0.1</sub>	0.63	0.3912	0.4222
PD 25	CaSO <sub>4</sub> : Mn <sub>5</sub> : Eu <sub>0.1</sub>	0.6495	0.3698	0.4166

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# TABLE 3.2

Values of activation energies calculated from Peeling Off decay curves for CaSO<sub>4</sub>:Mn:Eu phosphor

Sample No.	Description	Slowest exponential E <sub>1</sub> eV	Middle exponential E <sub>2</sub> eV	Faste <b>st</b> exponential E <sub>3</sub> eV
PD 15	CaSO <sub>4</sub> :Mn <sub>0.1</sub> :Eu <sub>0.01</sub>	0.5940	0.4690	,
PD 16	CaSO <sub>4</sub> :Mn <sub>0.1</sub> :Eu <sub>0.05</sub>	0.6340	0.5578	0.4590
PD 19	CaSO <sub>4</sub> :Mn <sub>0.1</sub> :Eu <sub>1</sub>	0.6213	0.4595	
2 P.D 4	CaSO <sub>4</sub> :Eu <sub>0.1</sub>	0.6992	0.5639	0.4511
PD 12	CaSO <sub>4</sub> :Mn <sub>0.1</sub> :Eu <sub>0.1</sub>	0.6153	0.4690	
PD 22	CaSO <sub>4</sub> :Mn <sub>0.3</sub> :Eu <sub>0.1</sub>	0.6284	0.4743	
PD 23	CaSO <sub>4</sub> :Mn <sub>0.5</sub> :Eu <sub>0.1</sub>	0.6291	0.5440	0.4590
PD 25	CaSO <sub>4</sub> :Mn <sub>5</sub> :Eu <sub>0.1</sub>	0.6329	0.5546	0.4610

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PLOTS OF Log I X Log t FOR Caso4 :Mn:Eu PHOSPHOR (ORIGIN IS DIFFERENT FOR DIFFERENT CURVE) PD 4 CaSO4: Eu 0.1 PD15 CaS04 : Mn 0.1 Eu 0.01 PD16 CaS04 : Mn<sub>0.1</sub> : Eu<sub>0.05</sub> PD19 CaSO4 : Mno.1: Eu1 Θ, Q 3.2 3.0 Õ 2.8 PD4 G 0 2.6 PD 19 2.4 . © 0 2.2 PD 16 2.0 **5** 1.8 PD15 1.6 1.4 1.2 1.0 0.8 0.6 0.4 0.2 (0.6,0) 0.7 0.8 0.9 1 1.1 1.2 1.3 1.4 1.5 1.6 1.7 1.8 1.9 2 2.1 2.2 3 log t 🛶 Fig 3.4

# 102

11-





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