
CHAPTER V

DISCUSSION OF RESULTS AND CONCLUSIONS

C H A P T E R V

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The results obtained from photo and thermoluminescence studies used to interpret them and to draw inferences regarding the traps and trapping process. Both the techniques yield information about the activation energy E and kinetics of the recombination process. In this chapter the discussion of results obtained in the present investigation is made.

5-1 NATURE OF DECAY;

The phosphorescence decay of long duration results from the release of electrons from metastable states (1,2,3) which serves as trapping states for electrons. The decay law may be exponential or hyperbolic depending upon the trap depths and their distribution. The exponential decay law represented by equation (3.4) and hyperbolic decay law is represented by equation (3.7). A straight line graph would result by plotting $\log I$ versus t and I versus t as per equation (3.4) and (3.7) respectively. From the present decay observations reveal that, plots of $\log I$ versus t (time) and I versus t are non-linear, indicating that the decay is not either exponential or hyperbolic. However, the plots of $\log I$ and $\log t$ (see fig.3.2 to 3.5) are found almost linear implying hyperbolic decay which can be represented by the equation of the type,

$$I_w = I_0 t^{-b} \quad - - - - \quad (5.1)$$

Where I is the intensity at time t , I_0 is the intensity at the start of decay and b is the decay constant.

The hyperbolic decay is explained on the basis of Randall and Wilkin (4) monomolecular superposition theory. According to this, the hyperbolic decay is a result of the superposition of exponentials corresponding to different traps which can be expressed by the equation,

$$I = I_0 \exp(-p_1 t) + I_{02} \exp(-p_2 t) + \dots + I_{0n} \exp(-p_n t) \dots \quad (5.2)$$

Where I_{0n} is the phosphorescence intensity due to electrons in traps of energy E_n and p_n is the transition probability of an electron escaping from a trap of depth 'n'.

5-2 Activation Energy From Decay Curves:

Each decay curve has been splitted up into three exponentials and the trap depths corresponding to these exponentials have been calculated by the 'peeling off' procedure. The trap depths thus calculated are listed in table 3.1. The values of trap depth of slowest exponentials are in good agreement with the values of trap depth obtained from glow curves. The agreement justifies the use of Randall and Wilkin's monomolecular superposition theory.

5-3 Distribution of Traps:

The distribution of traps may be uniform or quasi-uniform or exponential. The distribution of traps in the

present phosphor system can be ascertained as follows:

For an uniform trap distribution, when phosphorescence is greater than a few microseconds is given by

$$I(t) = nkT t^{-1} \quad \text{---} \quad (5.3)$$

However, obtained decay is of the form

$$I(t) = I_0 t^{-b} \quad \text{---} \quad (5.4)$$

The values of 'b' observed in the present investigation are found to be around 0.29. But according to equation (5.3), the value of 'b' would be unity. Thus the deviation from unity excludes the possibility of uniform trap distribution. Again the graph of log I versus t gives deviation from straight line which rules out possibility of exponential trap distribution. Therefore, the trap distribution, in present system, may be quasi-uniform.

5-4 Kinetics:

In the present system, observed decay follows the hyperbolic law and the slope is less than unity. This is represented by the equation (5.4). This rules out the monomolecular decay process represented by equation (3.4). The bimolecular decay is given by equation (3.7) is also excluded as the plot between \sqrt{I} and t represents the non linear in character. Again the value of slope would be -2 provided the graph is linear.

The present decay process is explained on the basis of monomolecular superposition theory suggested by Randall and Wilkin's (4). This superposition theory is useful to interpret the results. Hence the possible kinetics involved in the phosphorescence decay can be decided to be monomolecular.

5-5 Activation Energy From Glow Curves:

The activation energy from glow curves have been calculated using following different methods.

- 1) Initial rise method
- 2) Halperin and Braner's method
- 3) Grossweiner's Method.

The activation energies thus calculated are listed in table 4.2. From table it has been found that there is no systematic variation with the addition of flux concentration in the temperature range studied. The values of E calculated from these three methods are found to in mutual agreement. The small change in activation energy with the addition of flux concentration may be attributed to, within the single group of traps, there may exist subgroups which are probably very close to each other (5).

5-6 Escape Frequency Factor:

The escape frequency factor 'S' is evaluated using Randall and Wilkin's formula based on monomolecular kinetics (1). viz.,

$$\frac{\beta E}{kT_m^2} = S \exp. \left(- \frac{E}{kT_m} \right) \quad \text{--- (5.5)}$$



The values of E obtained from Halperin and Braner's formula were used in above equation to obtain 'S'. The S values thus obtained vary from 10^4 to 10^{14} Sec.^{-1} for sample studied and is listed in table 4.3. This is due to sensitiveness of formula to slight change in E values, i.e. a small change in E value results in large variation in S value.

5-7 Addition of Flux on Distribution of Trapping States:

Addition of flux does not change the form of decay and also does not give rise to new glow peaks in the temperature range studied. Moreover, the variation observed in the values of decay constant (b) and activation energy (E), which are trap parameters, is also very small and unsystematic. This indicates that the addition of flux only modifies the relative importance of traps responsible for phosphorescence decay and thermoluminescence but not their mean depth (6).

This implies that the trapping levels are not associated with activators but they are the defects in host lattice. These defects are likely to be Ca^{++} or S^{-} ion vacancies, and these vacancies might have ^{been} created during the synthesis of phosphor at high temperature (900°C). The probable reason for why Ca do not introduce new trapping levels might be Ca^{++} replaces Ca^{++} and these have same valency.

5-8 Kinetics of Thermoluminescence:

Halperin and Braner's method gives an insight into the types of kinetics involved in the thermoluminescence process.

In this method the parameter known as symmetry factor, $\mu_g = T_2 - T_m / T_2 - T_1$ which is a measure of the types of kinetics involved in the process.

The values of $\mu_g \leq e^{-1} (1 + \Delta)$ correspond to the monomolecular kinetics, while larger values to the bimolecular kinetics. The calculated values of μ_g are found to be greater than $e^{-1} (1 + \Delta)$ indicating the bimolecular process (see table 4.4). The values of μ_g particularly depends upon σ i.e. $T_2 - T_m$ and $\mu_g > e^{-1} (1 + \Delta)$ may arising from the broad distribution of traps on the high temperature side.

The values of E determined from three methods (1) Initial rise method (2) Halperin and Braner method (3) Method due to Grossweiner agree well with each other. The initial rise method is independent kinetics involved in thermoluminescence, while second and third methods are based on monomolecular kinetics. On comparison it may be seen that the values of E by above method agree well with each other suggesting that the kinetics involved to be monomolecular type. This contention is also supported by the phosphorescence decay study.

5-10 Conclusions:

The principal findings of the present investigation may be summarised as follows:

- 1) The phosphorescence decay follows the relation

$$I = I_0 t^{-b}$$

- 2) The decay curves are hyperbolic in nature and are explained on the basis of superposition theory of exponentials.
- 3) The probable kinetics involved in the luminescence process appears to be monomolecular.
- 4) The distribution of trapping states is likely to be non-uniform.
- 5) Small variation of activation energy with addition in flux percentage suggests that the change in flux percentage only modifies the relative importance of the traps but not their mean depth.
- 6) The variation in flux percentage does not introduce any new trapping levels which are effective within the studied temperature range.
- 7) The TL emission intensity is affected with the change in flux percentage. The TL emission is maximum in each series of flux at some concentration. This is attributed to the atoms of flux cluster around activator atom and bring about the changes in the number of centres.

5-11 REFERENCES:

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