CHAPTER V

GENERAL DISCUSSION AND CONCLUSIONS

This chapter is devoted to the general discussion of the results obtained in the present investigation. Although some interpretations and inferences drawn from specific studies,were described at the end of the preceding chapters, they are now summarized and further discussed.

5.1 NATURE OF DECAY:

The decay measurements reveal that, plots of log intensity (I) versus time (t) are nonlinear, indicating that the decay is not exponential. However, plots of log I versus log t are found almost linear, implying hyperbolic decay which can be represented by the equation of the type (1)

$$I = I_o \, t^{-b} \text{ - - - - - - - - - - - - } (5.1)$$

where I is the intensity at time t, I_o is the intensity at the start of decay, and b is the decay constant.

This hyperbolic decay is explained on the basis of Randall and Wilkins' (1) monomolecular theory, according to which, such a hyperbolic decay is a result of the superposition of exponentials corresponding to different traps which can be expressed by the equation,

$$I = I_{o1} \exp. (- P_1 t) + I_{o2} \exp. (-P_2 t) + \text{ - - - } + I_{on} \exp. (-P_n t) \text{ - - - - - - - } (5.2)$$

where Ion is the phosphorescence intensity due to electrons in trap of energy E_n and P_n is the transition probability of an electron escaping from a trap of depth E_n.

5.2 ACTIVATION ENERGIES 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 evaluated are found in good agreement with those obtained from glow curves. This agreement justifies the use of Randall and Wilkins' monomolecular superposition theory and hence the use of the fundamental equation,

$$P = S \exp. \left(-E/kT \right) \text{ - - - - - - - - - } (5.3)$$

for the present series of sulphide phosphors.

5.3 DISTRIBUTION OF TRAPPING STATES:

The distribution of trapping states is ascertained by using the relation

$$I = \frac{N\,kT}{t} \left[1 - \exp. (St) \right] \; ; \text{ - - - - - - } (5.4)$$

which, for uniform trap distribution, takes the form

$$I = I_o\, t^{-1}$$

In the present case, the power of t (the b value) is not unity or close to unity, and this rules out the possibility of uniform or quasiuniform trap distribution. However, on the other hand, the value of b, for all samples, is less than unity, indicating thereby that the trap distribution is likely to be non-uniform. Now refering to equation I = constant $t^{-(\beta kT+1)}$; [illegible], for an exponential trap distribution $b = (\beta kT + 1)$, which means $b > 1$ (2). For our samples, b fluctuates between 0.24 and 0.73 and this excludes the probability of exponential trap distribution.

Above conclusion is supported by a plot between I.t and log t obtained for present samples. The curves are neither straight lines parallel to log t axis nor exponential as required by uniform and exponential trap distributions respectively. However, they are increasing ones, suggesting trap distribution to be non-uniform. The curves thus obtained also give an idea about the density of traps at various depths.

5.4 GLOW CURVES:

It has been found that a glow curve for undoped SrS exhibits single peak in the temperature region studied. An addition of Zn does not give rise to new glow peak. However, when it is added in presence of flux (NaCl), an additional glow peak (around 325°K) is observed. The flux NaCl, when added alone, also found to give new glow peak (around 325°K).

5.5 ACTIVATION ENERGIES FROM GLOW CURVES:

The activation energies from glow curves have been calculated using four different methods: (1) Initial rise method, (2) Method due to Hoogenstraaten, (3) Halperin and Beraner's method, and (4) Grossweiner's formula. On comparison, it has been found that the activation energies thus obtained, agree resonably well (see Tables 4.1, 4.2).

5.6 ESCAPE FREQUENCY FACTOR:

The excape frequency factor S is evaluated using Randall and Wilkins' formula based on monomolecular kinetics (1) viz.

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

The values of E obtained from the Helperin and Braner's formula were used in above equation to obtain S. The S values thus obtained vary from 10^9 to 10^{22} Sec^{-1} for all samples. In some cases S values are found to be too high as compared to those repeated by other workers (3,4). This might be due to sensitiveness of formula to slight change in E value, i.e. a small change in E value results in large variation in S value.

5.7 EFFECT OF ADDITION OF Zn AND FLUX NaCl ON DISTRIBUTION OF TRAPPING STATES - THE NATURE AND ORIGIN OF TRAPS:

a) Unfluxed SrS: Zn Phasphors:

Measurements of phosphorescence decay and thermoluminescence reveal that the addition of activator (Zn) only modifies the relative importance of the traps responsible for phasphorscence and thermoluminescence, but not their mean depths (5). This implies that the traps in this phosphores are defects in host lattice. These defects are likely to be the Sr^{++} or S^{--} ion vacancies; since Sr^{++} and S^{--} intersitials are not possible [Interstitial radius of SrS = 0.73 A^{o}, Ionic radius of Sr = 1.13 A^{o}, Ionic radius of S = 1.84 A^{o}]. As pure SrS is nonluminescent these Sr & S vacancies might have created during the synthesis of phosphor at high temperature (900°C). The probable reson for why Zn do not introduces new trapping levels, might be the, Zn replaces the Sr and these two have the same valancy.

b) Phosphors Containing Flux (NaCl):

It has been found that when flux, NaCl, is added to the host lattice and its concentration is varied new trapping levels are introduced in the host lattice. Now on consideration of ionic radii of Sr, S, Na & Cl, Na^+ can replace Sr^{++} and Cl^- to S^{--}. This situation will cause to create additional defects to balance the charge. These additional defects might be acting as trapping states which are responsible for observed glow peak.

c) Fluxed SrS:Zn Phosphors:

Addition of Zn in presence of flux gives rise to new glow peak at high concentration of Zn. This can be understood as: when flux is incorporeted, Na replaces to Sr & Cl to S. If Zn is added to such a system some of the Zn atoms will replace the Na ions and this will creat the imbalance of charge. In order to maintain the balance of charge some additional defects will be created and these might be acting as trapping states.

5.8 KINETICS OF LUMINESCENCE:

The measurements of phosphorescence decay reveal that the observed nature of decay could be explained on the basis of monomolecular superposition theory thus indicating the kinetics to be monomolecular. In thermoluminescence studies, E values calculated on the assumption of the first order kinetics (E_{G_1} and E_{H_3}) agree most with Ei (independent of kinetics), again indicating the kinetics to be first order. However, E_{G_1} and E_{H_3} values do not agree with those estimated by Chen's method (general order of kinetics). Thus the order of kinetics thought to be monomolecular is suspicious.

The summetry factor $\mu g = \delta/W$, is also a characteristic of the type of kinetics involved in the process. The values of μg obtained for present glow peaks (listed in Table 4.2) are found to be greater than $e^{-1}\ (1 + \frac{2}{\Delta})$; indicating the kinetics to be bimolecular and thus contradicting the above conclusion. However, as discussed earlier (see section 4-22), any such conclusion drawn from the magnitude of μg is likely to be erroneous.

To establish a centainty in the result, another method is followed and is one proposed by Muntoni et.al (6). According to this method, a plot of log $\frac{I\ (T)}{[S\ (T)]^{\alpha}}$ versus $\frac{1}{T}$ results in a straight line for specific value of α, which represents the order of kinetics; while for other values it is being concave or convex. Here α, which represents the order of kinetics, is an idex of the integrated area of the curve in the interval from T to T_f ; T_f being the temperature corresponding to the end of the glow peak. For glow peaks of present samples, an average value of α comes to be 1.5 ± 0.2. Non-integer values of α were also observed by Muntoni et.al (6) for ZnS and

NaCl and by Kathurid and Sunta (7) for Lif TLD-100. Thus, taking into consideration non-agreement of E values and also unreliability of conclusions drawn from μg values, here it may be concluded that the kinetics involved in the luminescence process is not uniquely monomolecular or bimolecular, but likely to be intermediate whose order is about 1.5 ± 0.2.

5.9 SIZE OF TRAPS:

The size of traps has been evaluated in terms of capture cross-section σ, which is given by the equation

$$\frac{S}{\sigma} \simeq 1.5 \times 10^{26} \quad \text{- - - - - - - - - -} \quad (5.6)$$

It has been found that the value of σ, estimated by making use of S values obtained from Randall and Wilkins' formula, vary from 1.66×10^{-16} to 1.29×10^{-4} Cm^2. The traps of present investigation can be regarded as giant traps (8).

5.10 MECHANISM OF ENERGY TRANSFER:

The transfer of energy from absorption centre to the emitting one can take place by any one or more processes of the following:

1) Quantum mechanical resonance process,
2) Cascade mechanism,
3) Exciton migration, &
4) With movement of charge carriers.

If quantum mechanical resonance process is operative then, according to Garlik (2), for energy transfer with electric dipole field overlap the value of life time (τ) is of the order of 10^{-6} Sec^{-1}, and for quadrupole or magnetic dipole field overlap it is $\geq 10^{-4}$ Sec^{-1}. In the present case the value of τ are found to be greater than 10^{-4} Sec^{-1}, indicating the transfer of energy is accomplish by a quadrupole or magnetic dipole field overlap. As in the present system of phosphors motion of electrons is involved (release of electrons from traps and their recombination with luminescence centre) the transfer of energy with movement of charge carriers is also a possible mechanism.

From present studies it is not possible to acertain whether cascade and execiton migration mechanisms are operative or not. Since this will need additional studies, such as absorption and fluroscence spectra, which are beyond the scope of present work.

5.11 CONCLUSIONS:

The main conclusions drawn from the present study may be summarised as follows:

(1) Phosphorescence decay is of the form

$$I = Io\ t^{-b}$$

(2) The decay is hyperbolic in nature and can be explained in terms of superposition of exponentials.

(3) The fundamental equation $p = S \exp. \left(\frac{-E}{kT} \right)$ holds good in the present system of phosphors.

(4) The distribution of trapping states is likely to be non-uniform.

(5) Incorporation of Zn in to the SrS do not introduces new trapping levels, but when it is added in presence of flux, new trapping levels are created.

(6) Addition of flux, NaCl, to the SrS gives rise to new trapping levels.

(7) Traps of energy $E = 0.60$ eV, are due to the defects in host lattice and these defects are likely to be the Sr^{++} or S^{--} ion vacancies. These might have created during the synthesis of phosphor at high temperature (900°C).

(8) Average size of traps is of the order of 10^{-10} Cm^2 and traps may be termed as giant traps.

(9) The probable type of kinetics involved in the luminescence process is not uniquely monomolecular or bimolecular, but likely to be intermediate whose order is about 1.5 ± 0.2.

(10) Probably, the transfer of energy is accomplished by a quantum mechanical resonance process (quadrupole or magneticdipole field overlap) as well as by a movement of charge carriers.

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5.12 REFERENCES:

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