
CHAPTER - V

GENERAL DISCUSSION AND CONCLUSIONS

C H A P T E R - 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 the plots of logarithm of intensity (I) versus log t are almost linear implying decay to be hyperbolic which can be represented by the equation of the type (1).

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

Where I is the intensity at time t, I_0 is that at the start of the 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 various exponentials corresponding to different traps and can be expressed by the equation,

$$\begin{aligned} I &= I_0 t^{-b} \\ &= I_{01} \exp. (-p_1 t) + I_{02} \exp. (-p_2 t) + \dots \\ &\quad \dots \quad + I_{0n} \exp. (-p_n t) \quad (5.2) \end{aligned}$$

Where I_{on} is the phosphorescence intensity due to electrons in the 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 two exponentials (2) 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,

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

for the present series of sulphide phosphors. The E values thus calculated for slowest and for fastest exponentials vary from 0.74 eV to 1.30 eV, from 0.63 eV to 1.18 eV respectively.

5-3 DISTRIBUTION OF TRAPPING STATES:

The distribution of trapping states is ascertained by using the relation,

$$I = \frac{NkT}{t} [1 - \exp.-(St)], \quad - - - - (5.4)$$

Which for uniform trap distribution takes the form

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

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 quasi-uniform 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 referring to equation

$I = \text{constant } t^{-(\beta kT + 1)}$ for an exponential trap distribution $b = (\beta kT + 1)$, which means $b > 1$. For our samples, b fluctuates between 0.13 and 0.20 and this excludes the possibility of exponential trap distributions.

Above conclusion is supported by a plot between $I \cdot t$ and $\log t$ obtained for the 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 contributing to the phosphorescence decay.

5-4 GLOW CURVES:

All the samples exhibit two glow peaks. However, for most of the samples second glow peak appears at the temperature

beyond the range of study. The peak positions and the general features of the glow curves are affected by the addition of activator, but the observed change is not systematic in nature.

5-5 ACTIVATION ENERGIES FROM GLOW CURVES:

The activation energies corresponding to both the glow peaks have calculated by the methods : (i) Method due to Halperin and Branner, (ii) Method due to Grossweiner, (iii) Method due to Garlick and Gibson (initial rise method), and (iv) Method due to Urbach. It has been found that the activation energies thus obtained are consistent (see Tables 4.1 and 4.2).

A comparison of E values determined from thermoluminescence studies with those obtained from decay measurements carried on the same samples indicates that the energies corresponding to first glow peak are in close agreement with slowest exponential of decay. The E values corresponding to second glow peak are being considerably high. Thus indicating that, to investigate deeper traps one has to adopt TL technique rather than the decay.

5-6 ESCAPE FREQUENCY FACTOR:

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

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

The value of E obtained from Halperin and Branner's formula were used in above equation to obtain S . The S values thus obtained vary from 10^8 to 10^{18} Sec^{-1} for all samples. In some cases S values are found to be high as compared to those reported 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 values (3).

The values of escape frequency factor (S) and size of traps (σ) for 1st and 2nd glow peaks are listed in Tables 4.3 and 4.4. Looking to the values of size of traps the traps may be termed as giant traps (4).

5-7 EFFECT OF ADDITION OF ACTIVATOR ON TRAP PARAMETERS:

Addition of activator (Pb) does not change the form of decay (see Fig. 3.1 to 3.3) and also does not give rise to new glow peaks in the temperature region studied (Fig. 4.1 to 4.6). Moreover, the variation observed in values of both decay constant (b) and activation energy (E), which are the trap parameters, is also negligibly small. This indicates that the addition of activator only modifies the relative importance of traps responsible for phosphorescence decay and thermoluminescence but not their mean depths (5,6).

5-8 NATURE AND ORIGIN OF TRAPS:

As mentioned earlier (Section 5-6) incorporation of activator (Pb) into the host lattice does not give rise to

to new glow peaks in the temperature region studied and also does not change the mode of decay. Moreover, variation observed in the trap parameters with activator concentrations is negligible. This indicates that the trapping levels are not associated with activator but they are likely to be the defects in the host lattice (6,7).

The defects present in CaS may be either vacancies (cation or anion) or interstitials. However, on atomic size considerations (ionic radii of $\text{Ca}^{2+} = 0.99 \text{ \AA}$, $\text{S}^{2-} = 1.84 \text{ \AA}$ and interstitial radius^s of CaS = 0.61 \AA), one can say that sulphur ion is too large to be accommodated in an interstitial site. Similarly the calcium ion interstitials are very much unlikely. The only possibility left is the defect arising due to calcium or sulphur ion vacancies. The previous studies reported (8,9) from Shivaji University laboratory and studies by Ekbote and Ranade (10) on CaS phosphors indicate that the sulphurisation of phosphors causes a reduction in trapping levels. Thus, the trapping levels in present phosphor system may be attributed to the S vacancies. Such vacancies have been observed by Ghosh and Shankar (11) in the EPR studies on polycrystalline CaS. According to them, there exists two types of vacancies: one is a single vacancy - S ion vacancy surrounded by six Ca ions as its nearest neighbours and other is a divacancy - S ion vacancy having one Ca ion vacancy as one of the nearest neighbours.

During irradiation with UV, electrons from lattice are excited to these defects and are captured there which in turn give luminous emission. However, from present measurement it is not possible to attribute a particular vacancy to a particular glow peak or a decay component. Trapping states in these phosphors exist prior to irradiation and these might have created during the synthesis of phosphor at high temperature.

5-9 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_{H_1} and E_{G_1}) agree most with E_i (independent of kinetics), again indicating the kinetics to be monomolecular.

The symmetry factor $\mu_g = \frac{\delta}{W}$ is also a characteristic of the type of kinetics involved. The μ_g values are not consistently greater or less than $e^{-1} \left(1 + \frac{2}{\Delta} \right)$, indicating thereby that some of the glow peaks belong to first order while remaining ones to second order. However, many times, presence of broad distribution of trapping levels and/or weak shoulders at high temperature side of a glow peak causes

an apparent increase in μg values and any such conclusion drawn from the magnitude of μg is likely to be erroneous.

To establish a certainty in the results, a method due to Mutoni et al (12) is followed and is based on kinetic equation. According to this method, the value of α which results in a linear plot between $\log \frac{I(T)}{[S(T)]^\alpha}$ and $\frac{1}{T}$ represents the order of kinetics. In the present case, the value of α comes to be 1.5 ± 0.3 . Thus taking into considerations the agreement of E values and unreliability of conclusions drawn from μg values, here, it may be concluded that the possible kinetics involved in the luminescence process is either monomolecular or intermediate ($\alpha = 1.5 \pm 0.3$).

¹⁰
5-9 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) Excitation migration, and
- 4) With movement of charge carriers.

If quantum mechanical resonance process is operative, then according to Garlick (13), for energy transfer with electric dipole field overlap, the value of transition

probability is of the order of 10^{-6} Sec^{-1} , and for quadrupole or magnetic dipole field overlap it is $\geq 10^{-4} \text{ Sec}^{-1}$. In the present case the values of transition probabilities are of the order of 10^{-4} Sec^{-1} , indicating that the transfer of energy is accomplished 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 centres), the transfer of energy with movement of charge carriers is also a possible mechanism.

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

5-¹¹~~10~~ CONCLUSIONS:

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

- 1) Phosphorescence decay is of the form $I = I_0 t^{-b}$.
- 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) Addition of activator (Pb) only modifies the relative importance of traps responsible for phosphorescence and thermoluminescence, but not their mean depths.
- 6) Traps are due to the defects in the host lattice.
- 7) Defects present in the host lattice are likely to be sulphur ion vacancies and these might have created during the synthesis of phosphor at high temperature.
- 8) Average size of the traps is of the order of 10^{-12} cm² and traps may be termed as giant traps.
- 9) The possible type of kinetics involved in the luminescence process is either monomolecular or intermediate.
- 10) Probably, the transfer of energy is accomplished by a quantum mechanical resonance process (quadrupole or magnetic dipole field overlap) as well as by a movement of charge carriers.

REFERENCES:

1. Randall, J. T. and Wilkins, M. H. F., Proc. Roy. Soc. A 184, 366 (1945).
2. Mor, S. L. and Bhawalkar, D. R., Indian J. Pure and Applied Phys. Vol. 8, 320 (1970).
3. Kathuria, S. P. and Sunta, C. M. J. Phys. D: Appl. Phys., 12, 1 (1979).
4. Lax, M., Phys. Rev., 119, 1502 (1960).
5. Lawangar, R. D. and Narlikar, A. V., Luminescence, 11, 135 (1975);
6. Sinha, O. P. and Sivayaman, S., Indian J. Pure. Appl. Phys., 10, 134 (1972).
7. Jain, S. C., and Bhawalkar, D. R., Indian J. Pure Appl. Phys., 13, 74.
8. Lawangar, R. D. and Narlikar, A. V., J. Mat. Sci., 10, 1251 (1975).
9. Shalgaonkar, C. S., Lawangar, R. D., Pawar S. H., Narlikar, A. V., Mat. Res. Bull., 12, 525 (1977).
10. Ekbote, S. N. and Ranade, J. D. Indian J. Phys., 45, 529 (1972).
11. Ghosh, P. R. and Shankar, V., J. Luminescence, 20, 139 (1979).
12. Muntoni, C. Rucci, A., and Serpi, A., Ricevs Sci., 38, 762 (1978).
13. Garlik, G. F. T. Encyclopedia of Physics, Edt. by S. Fugg. Vol. XXVI, light and matter II, edition (1958).