

**CHAPTER - V**

**GENERAL DISCUSSION AND CONCLUSIONS**

## CHAPTER - V

### GENERAL DISCUSSION AND CONCLUSIONS

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

#### 5.1 GLOW CURVES :

The thermoluminescence measurements have been carried out in the temperature range of 300°K to 510°K and the observed glow curves of almost all samples found to exhibit two peaks - one around 380°K and other 467°K. It has been found that the glow curves depend sensitively upon the concentrations of Bi and Mn. The shape and relative peak heights, and positions of glow curves are significantly influenced by both Bi and Mn concentrations but in an unsystematic manner. Moreover, addition of activators Bi and Mn does not found to give new glow peaks in the temperature region studied. From these results the conclusion to be drawn is that the addition and changing concentrations of Bi<sup>3+</sup> and Mn<sup>2+</sup> either alone or in presence of each other probably affect the relative population of traps and shift the centre of gravity of trapping states (1,4,11) but in an unsystematic manner.

## 5.2 ACTIVATION ENERGY FROM GLOW PEAKS :

The activation energies corresponding to all glow peaks have been evaluated by the methods (i) method due to Grossweiner, (ii) method due to Halperin and Branner, (iii) method due to Chen, and (iv) method due to Urbach. It has been found that the activation energies thus obtained are consistent (see table 3.1 to 3.5).

## 5.3 ESCAPE FREQUENCY FACTOR :

Escape frequency factors  $S$  is evaluated using Chen's formula based on the second order kinetics viz.,

$$S = \frac{\beta \left(\frac{E}{KT_m}\right)^2 \exp. \left(\frac{E}{KT_m}\right)}{T_m \left(\frac{E}{KT_m} + 2\right)} \quad \dots (5.1)$$

The values of  $E$  obtained from Halperin and Branner's formula (second order) were used in above equation to obtain 'S'. The  $S$  values thus obtained vary from  $10^6$  to  $10^{15} \text{ sec}^{-1}$  for all samples. The observed variation is not systematic with respect to change in percentage of activator concentration. However, no definite significance can be attached to variation in  $S$  values unless these are determined by method independent of  $E$ . This is since, a change of few percent of  $E$  would change the  $S$  value by orders of magnitude. Therefore, it appears here that the large variation in  $S$  are a consequence of differing values of  $E$ . The findings of Kathuria and Sunta (2) favour the view point.

#### 5.4 EFFECT OF ACTIVATORS ON TRAP PARAMETERS :

Addition of activators ( $\text{Bi}^{3+}$ ,  $\text{Mn}^{2+}$ ) does not give rise to new glow peaks in the temperature region studied (see figures 3.1 to 3.4). Moreover, the activation energies corresponding to various peaks do not vary significantly with activator concentrations. The observed variation is also unsystematic in character. This indicates that the addition of activators only modifies the relative importance of traps responsible for thermoluminescence but not their mean depths (3,4).

Furthermore, the 'S' values for various samples containing varying concentration of activators are shown in table 3.6. The observed variation is not systematic with respect to activator concentration. However, no definite significance can be attached to this variation.

#### 5.5 NATURE AND ORIGIN OF TRAPS :

The addition of activators  $\text{Bi}^{3+}$  and  $\text{Mn}^{2+}$  do not introduce new trapping levels. Moreover, variation observed in trap parameters (E and S) with activator concentrations is negligible and unsystematic. This suggests that the trapping levels are not associated with activators but they are the defects in the host lattice. These defects are probably the  $\text{Ca}^{2+}$  and  $\text{O}^{2-}$  vacancies or interstitials created during the synthesis of phosphor at high temperature (5,6,16).

#### 5.6 KINETICS OF THERMOLUMINESCENCE :

The 'E' values calculated on the assumption of second order kinetics ( $\text{EH}_2$  and  $\text{EG}_2$ ) found to agree most with  $\text{EC}_2$  (general order

kinetics), indicating the kinetics to be second order.

The symmetry factor  $\mu g = \delta/W$  is also a characteristic of the type of kinetics involved in the process. The values of  $\mu g$  obtained are greater than  $e^{-1} (1 + \Delta)$ , which again indicates the kinetics to be second order.

Thus, here it may be concluded that the kinetics of thermoluminescence process is likely to be second order.

#### 5.7 X-RAY DIFFRACTION STUDIES :

Lehmann (5) has reported that CaO crystallizes in the same cubic NaCl lattice as CaS. The X-ray diffraction pattern of CaO prepared by thermal reduction method in the present investigation shows a face centered cubic structure with lattice constant 'a' equal to 8.71 Å°. The analysis of XRD pattern obtained for fluxed CaO:Bi:Mn samples found to show the face centered cubic structure.

#### 5.8 DEPENDENCE OF XRD INTENSITY ON ACTIVATOR CONCENTRATION :

The variation of XRD intensities as a function of concentrations of  $\text{Bi}^{3+}$  and  $\text{Mn}^{2+}$  either alone or in presence of each other has been studied for planes (111), (220), (422) and (622). The intensity initially increases, reaches to a maximum at certain concentration and then decreases. The concentration at which maximum intensity observed is 0.1 wt % of  $\text{Bi}^{3+}$  or  $\text{Mn}^{2+}$ . No systematic variation is observed with concentration of  $\text{Bi}^{3+}$  when added alone.

### 5.9 VARIATION OF LATTICE CONSTANT WITH ACTIVATOR CONCENTRATION :

The variation of lattice constant with activator concentrations of  $\text{Bi}^{3+}$  and  $\text{Mn}^{2+}$  in presence of each other found to exhibit a systematic variation. The lattice constant initially decreases, reaches to a minimum at certain concentration and then increases. The concentration at which minimum lattice constant observed is 0.1 wt % of  $\text{Bi}^{3+} / \text{Mn}^{2+}$ . It should be mentioned that no systematic variation has been observed with concentration of  $\text{Bi}^{3+}$  or  $\text{Mn}^{2+}$  when added alone.

### 5.10 POSITION OF $\text{Bi}^{3+}$ AND $\text{Mn}^{2+}$ IN CaO LATTICE :

The addition of  $\text{Bi}^{3+}$  and  $\text{Mn}^{2+}$  in CaO lattice probably take the  $\text{Ca}^{2+}$  sites. This is because ionic radii of  $\text{Ca}^{2+}$ ,  $\text{Bi}^{3+}$  and  $\text{Mn}^{2+}$  are 0.99 Å, 0.98 Å and 0.93 Å respectively. The difference in ionic radii is within 15% and as such  $\text{Bi}^{3+}$  and  $\text{Mn}^{2+}$  can take easily  $\text{Ca}^{2+}$  positions at the lattice site.

### 5.11 ELECTRON PARAMAGNETIC RESONANCE STUDIES :

The EPR measurement of prepared samples are carried out with a view to gain the information about the defect structure responsible for luminescence properties. However, in all studied samples the characteristic  $\text{Mn}^{55}$  spectrum is observed.

The EPR measurements of samples containing  $\text{Bi}^{3+}$  and  $\text{Mn}^{2+}$  exhibit similar nature consisting of six hyperfine lines of  $\text{Mn}^{55}$  corresponding to the transitions  $M = +\frac{1}{2} \rightarrow -\frac{1}{2}$ . The spin Hamiltonian parameter of Mn has been calculated and it is found to be in good agreement with

the results of other workers (12,14). The calculated value of 'g' varies between 1.99774 to 2.00695, but the observed variation is unsystematic and insignificant. The hyperfine splitting factor is nearly constant. The line width varies from 2.5 to 15 gauss but the observed variation is unsystematic.

#### 5.12 EFFECT OF TEMPERATURE ON EPR SPECTRUM :

The EPR measurements of prepared samples have been carried out at liquid N<sub>2</sub> temperature. It has been found that the change in temperature affects the nature of the spectrum. The EPR spectrum range at L.N.T. is from 2980 to 3440 gauss, while at room temperature it is 3160 to 3610 gauss. No effect of temperature is found on intensity of the signal and hyperfine splitting factor. However, with concentration of Mn the line width is found to increase, while with concentration of Bi it remains constant.

#### 5.13 CONCLUSIONS :

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

- 1) Glow curves depend sensitively upon the concentration of Bi and Mn. The shape and relative peak heights are significantly influenced by both Bi and Mn concentrations, but the observed change is not systematically in nature.
- 2) Addition of activators does not give rise to new glow peaks in the temperature region studied.

- 3) The variation of activation energies with activator concentration (Bi, Mn) is insignificant and unsystematic in character.
- 4) Probably the traps are defects in CaO lattice and are likely to be  $\text{Ca}^{2+}$  and  $\text{O}^{-2}$  vacancies or interstitials created during the synthesis of phosphor at high temperature.
- 5) Probable type of kinetics involved in thermoluminescence process is likely to be second order.
- 6) The prepared CaO : Bi : Mn phosphors crystallize in face centered cubic lattice with lattice constant  $a = 8.71 \text{ \AA}$ .
- 7) The XRD intensity is found to be sensitive to addition of activator concentrations of Bi and Mn. The intensity is maximum for optimum concentration 0.1 wt. %.
- 8) The lattice constant is found to be sensitive to addition of activator concentration of Bi and Mn. The lattice constant is minimum for optimum concentration 0.1 wt %.
- 9) The EPR spectrum of studied samples exhibits dominant six hyperfine lines of Mn.
- 10) There is no significant change in 'g' values.
- 11) The general nature <sup>of</sup> EPR spectrum is influenced by change in temperature.
- 12) There is no effect of temperature on intensity of the signal and on hyperfine splitting factor.
- 13) The activators Bi and Mn probably take the  $\text{Ca}^{++}$  position in CaO lattice.
- 14) CaO is versatile as a phosphor host.

REFERENCES

- 1 Sinha, O.P. and Sivaraman, S., Indian J. Pure Appl. Phys., 10, 134 (1972).
- 2 Kakthuria, S.P. and Sunta, C.M., J. Phys. D. Appl. Phys. 12, 1 (1972)
- 3 Lawangar, R.D. and Narlikar, A.V., J. Luminescence, 11, 135 (1975)
- 4 Jain, S.C. and Bhawalkar, D.R., Indian J. Pure Appl. Phys., 613, 74 (1975).
- 5 Lehmann, W.J., Luminescence, 6, 455 (1973).
- 6 Khare, R.P. and Ranade, J.D., Indian Journal of Pure and Appl. Phys., 13, 664 (1975).
- 7 Khare, R.P. and Manjula Srivastava, Indian J. Phys., 50, 702 (1976).
- 8 Shankar, V., et.al. Indian J. Pure Appl. Phys., 14, 193 (1976).
- 9 Uehara, Y.J., Chem. Phys., 50, 961 (1969).
- 10 Ghosh, P.K. and Shankar, V., Indian J. Phys. 53A, 203 (1978).
- 11 Patil, M.G., Ph.D. Thesis, Shivaji University, Kolhapur (1981).
- 12 Hadgal, R.R., Ph.D. Thesis, Shivaji University, Kolhapur (1982).
- 13 Lehmann, W.J., Luminescence, 20, 95 (1979).
- 14 Awate, A.V., Ph.D. Thesis, Shivaji University, Kolhapur (1975).
- 15 Mali, C.S., M.Phil. Thesis, Shivaji University, Kolhapur (1986).
- 16 Kolekar, M.J., M.Phil. Thesis, Shivaji University, Kolhapur (1988)

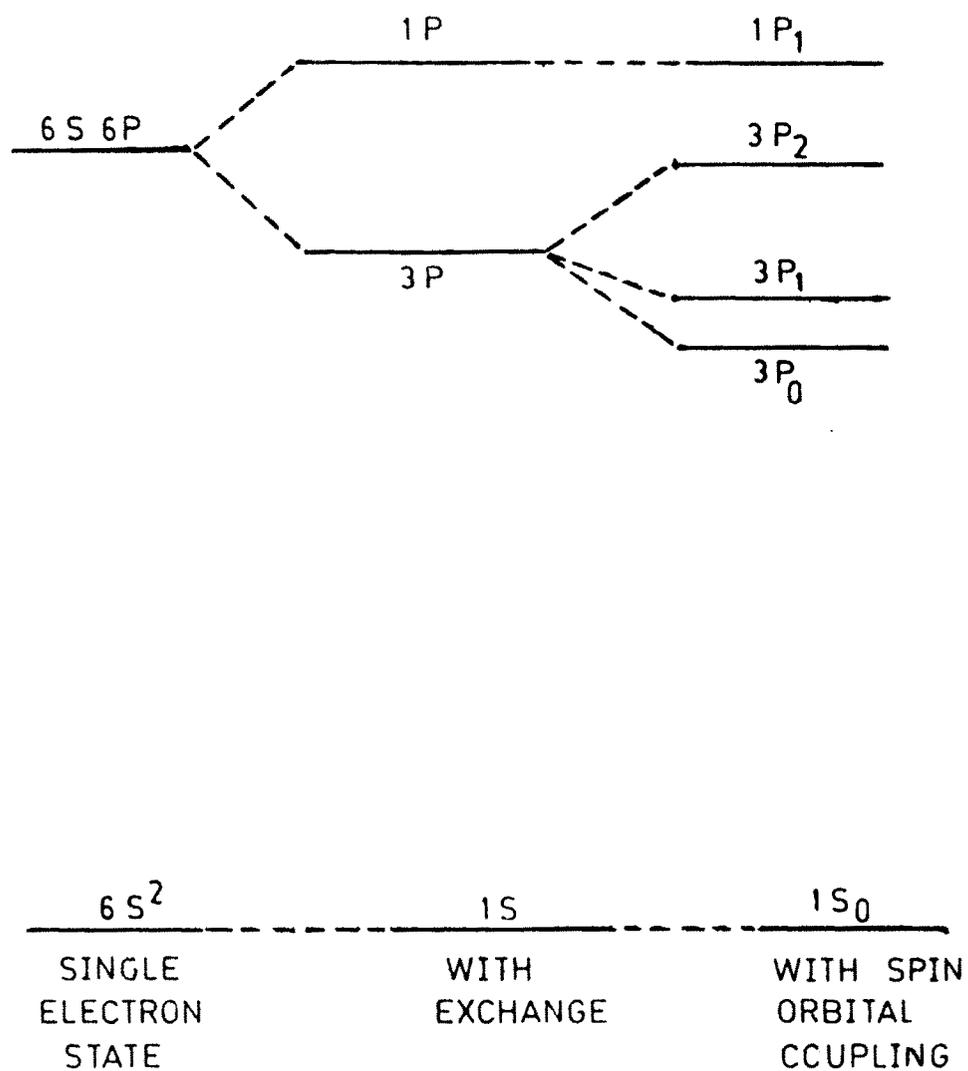


FIG. 5-1: ENERGY LEVELS OF THE FREE  $\text{Bi}^{3+}$  ION