
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 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 glow curves of all studied samples found to exhibit three peaks around 340°K, 380°K and 410°K. The general features and relative peak heights of glow curves are significantly affected by the Bi^{3+} and Ce^{3+} concentrations. However, no new glow peak is observed with addition and changing concentrations of Bi^{3+} and Ce^{3+} . Moreover, it has been found that at higher concentrations of Bi^{3+} and Ce^{3+} , there is tendency of merging of two groups of deeper traps and to enhance the population of resulting glow peak. From these results, the conclusion to be drawn is that the addition and changing concentrations of Ce^{3+} and Bi^{3+} either alone or in presence of each other, do not introduce new trapping levels but probably affect the relative population of traps and with shift in the centre of gravity of trapping states responsible for thermoluminescence. (1,4,11).

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 Braner, (iii) method due to Chen, and (iv) method due to Urbach. It has been found that the activation energies thus obtained are consistent (see tables 3.1 - 3.6).

5.3 ESCAPE FREQUENCY FACTOR :

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

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

The values of E obtained from Halperin and Braner's formula (second order) were used in above equation to obtain 'S'. The S values thus obtained vary from 10^8 to 10^{16} 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 per cent 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 (Bi^{3+} , Ce^{3+}) does not give rise to new glow peaks in the temperature region studied (See figs. 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 3.7. 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 :

Addition of activators (Bi^{3+} and Ce^{3+}) found to sensitively affect the peak intensity and peak position of the glow curves, but they 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 Ca^{2+} and 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 (E_{H2} and E_{G2}) found to agree most with E_{C2} (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 μ_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 EMISSION CHARACTERISTICS - ORIGIN OF SPECTRAL BANDS AND NATURE OF LUMINESCENCE CENTRES :

(a) Fluxed CaO :

It has been found that fluxed CaO exhibits bands at about 4360 Å⁰, 4750 Å⁰ and 5890 Å⁰. The bands at about 4360 Å⁰ and 4760 Å⁰ are weaker than 5890 Å⁰ band. The 5890 Å⁰ band is invariably observed for all samples and it has been attributed to Mn²⁺ impurity. The detail discussion is left to the next section. The unfluxed and undoped CaO did not show emission, the bands at about 4360 Å⁰ and 4750 Å⁰ could be attributed to fluxed CaO host lattice (9).

(b) Fluxed CaO : Bi :

The emission spectra of CaO : Bi phosphors found to exhibit bands peaking at about 4360 Å⁰, 4750 Å⁰ and 5890 Å⁰. The electron configuration of Bi atom is 1s², 2s², 2p⁶, 3s², 3p⁶, 3d¹⁰, 4f¹⁴, 5s², 5p⁶, 5d¹⁰, 6s², 6p³ and the ground states of free ion is 1s⁰. Bi³⁺ enters in trivalent states losing 6p³ electrons. The first excited state is due to 6s, 6p electron configuration and that is p state. According to L-S coupling scheme and Hund's rule the p state is further split into ³P₀, ³P₂ and ¹P₁ (7). Transitions between these levels take place in accordance with the selection rule

$\Delta J = \pm 1$. Consequently, the possible allowed transitions are $^1P_1 \longrightarrow ^1S_0$ and $^3P_1 \longrightarrow ^1S_0$ and the forbidden transitions are $^3P_2 \longrightarrow ^1S_0$ and $^3P_0 \longrightarrow ^1S_0$. The energy level diagram alongwith allowed and forbidden transition is shown in fig. (5.1). The allowed transitions i.e. $^1P_1 \longrightarrow ^1S_0$ and $^3P_1 \longrightarrow ^1S_0$ should give emission at about 4470 \AA^0 and 5120 \AA^0 respectively (7,8). The emission corresponding to transition $^1P_1 \longrightarrow ^1S_0$ is observed, but it is found to overlap on 4360 \AA^0 band of fluxed CaO. The variation of 4360 \AA^0 band intensity with Bi^{3+} concentration favours the view point. We could not observe band corresponding to 5120 \AA^0 . It is likely that it might have emitted but absorbed by some other centers.

(c) Fluxed CaO : Ce :

It has been found that the emission spectra of CaO : Ce phosphors exhibit bands at about 4360 \AA^0 , 4750 \AA^0 and 5890 \AA^0 . The band intensities have been significantly affected by Ce concentration without alteration in band positions. On considering the energy level diagram of Ce^{3+} atom (see fig. 5.2), the allowed transitions are

$$\begin{aligned} &^2D_{5/2} \longrightarrow ^2F_{7/2} \quad (6390 \text{ \AA}^0), \\ &^2D_{3/2} \longrightarrow ^2F_{5/2} \quad (5820 \text{ \AA}^0) \quad \text{and} \\ &^2D_{5/2} \longrightarrow ^2F_{5/2} \quad (5560 \text{ \AA}^0) \end{aligned}$$

In fact, one should observe these wavelengths in emission spectra. The emission corresponding to transition $^2D_{5/2} \longrightarrow ^2F_{7/2}$ might have emitted but it lies outside the range of our measurements. The 5820 \AA^0 emission might be overlapping on 5890 \AA^0 band. We could not observe a band corresponding to 5560 \AA^0 . It is likely that it might have emitted but absorbed in host lattice defects.

(d) Fluxed CaO : Bi : Ce :

The results obtained with addition and changing concentration of Bi^{3+} in presence of Ce^{3+} are similar to that of Bi^{3+} added alone. However, when Ce^{3+} is added in presence of Bi^{3+} , it is found that the band at about 4750 \AA° disappears and a new band around 5000 \AA° appears. The position and peak intensity of this new band is found to be sensitively affected by Ce^{3+} concentration but in an unsystematic manner (see fig. 4.3). The origin of this new band may be a luminescence centre formed by Ce^{3+} impurity in co-operation with host lattice defects responsible for emission of 4750 \AA° band.

5.8 ORIGIN OF 5890 \AA° BAND :

The intense emission band around 5890 \AA° is found invariably for all samples. The same band was also observed by many workers in undoped CaS and ZnS (7,10,11,12,13). Lalita et. al (14) reported that the deliberate addition of Mn^{2+} to CaS substitutes for Ca^{2+} to Mn^{2+} and gives rise to an emission band at about 5890 \AA° . Moreover, Lehman (15) and Hadgal (13) have reported that the undoped CaS and ZnS contain Mn^{2+} as trace impurity and it is responsible for emission at 5890 \AA° . EPR spectra of doped and undoped CaO phosphors (16) clearly show the presence of Mn^{2+} suggesting thereby the band at about 5890 \AA° is a characteristic of Mn^{2+} impurity, which might be present as a trace impurity in starting materials. This view is supported by the results of Shankar et. al (10) on CaS phosphors.

5.9 POSITION OF Bi^{3+} AND Ce^{3+} IN CaO LATTICE :

The addition of Bi^{3+} and Ce^{3+} in CaO lattice probably take the Ca^{2+} sites, this is because atomic radii of Ca^{2+} , Bi^{3+} and Ce^{3+} are 1.97 \AA , 1.70 \AA , and 1.81 \AA respectively. Difference in atomic radii is within 15% and as such Bi^{3+} and Ce^{3+} can take easily Ca^{2+} positions at the lattice site.

5.10 CONCENTRATION QUENCHING :

It has been found that the intensities of emission bands initially increase with activator (Bi, Ce) concentration, reach to a maximum value and then decrease with further increase in activator concentration. Also in thermoluminescence studies, the TL glow intensity initially found to increase with activator concentration and finally become very poor after reaching to a maximum value.

The observed effect is termed as concentration quenching phenomenon and could be explained on the basis of a model proposed by Johnson and William (17). Suppose that an activator atom, which was absorbed an incident photon, returns to the ground state with emission of a photon only if there is no other activator atom within a sphere of radius R around the central activator atom. In other words, we assure that the activator atoms interact with each other in such a way that if the distance between them is $\leq R$, they quench each other. Thus around a given activator ion let there be Z metallic positions within the sphere of radius R ; if any of these Z positions is occupied by another activator ion X , we assume that neither of them will act as a luminescence centre. Due to the quenching effect then η (luminescence efficiency) will be proportional to $C(1-C)^2$, where C represents the probability that a given metallic site is occupied by an activator

ion X. Furthermore, η will be proportional to the probability that a photon absorbed by the material as a whole is actually absorbed by an activator ion X; this probability is given by an expression of the type

$$\alpha C / [\alpha C + \beta (1-C)] = C / [(C + C\beta/\alpha)(1-C)] \quad \dots \quad (5.2)$$

where β/α is the ratio of the capture cross section of a photon of given wavelength by a lattice atom and by an activator ion X. Evidently, the ratio β/α will be a function of the wavelength of the exciting radiation; it also depends on temperature. Thus,

$$\eta = \frac{C (1-C)^2}{C + (\beta/\alpha)(1-C)} \quad \dots \quad (5.3)$$

For small concentration of the activator, η increases proportionally with C; at high concentrations, the mutual quenching takes over, leading to a decrease in η .

The present phosphor system exhibits the concentration quenching effect and almost satisfies the equation (5.3).

5.11 CONCLUSIONS :

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

1. The general features of the glow curves are sensitively affected by the concentrations of Bi^{3+} and Ce^{3+} .
2. Addition of activators Bi^{3+} and Ce^{3+} does not introduce new trapping levels but probably affects the relative population of traps and causes to shift center of gravity of trapping states responsible for thermoluminescence.

3. Probably the traps are defects in CaO lattice and are likely to be Ca^{2+} and O^{2-} vacancies or interstitials created during the synthesis of phosphor at high temperature.
4. Probable type of kinetics involved in thermoluminescence process is likely to be second order.
5. Undoped but fluxed CaO exhibits bands at about 4360 \AA , 4750 \AA and 5890 \AA .
6. The band at about 5890 \AA is probably due to Mn^{2+} trace impurity.
7. Addition of Bi^{3+} and Ce^{3+} into CaO sensitively affects the emission characteristics.
8. Addition of Bi^{3+} alone or in presence of Ce^{3+} gives its own characteristic emission.
9. Addition of Ce^{3+} alone or in presence of Bi^{3+} gives its own characteristic emission.
10. Addition and changing concentration of Bi^{3+} and Ce^{3+} exhibits the concentration quenching effect.
11. Bi^{3+} and Ce^{3+} probably takes the lattice site positions by replacing Ca^{2+} ions.
12. CaO is versatile as a phosphor host.

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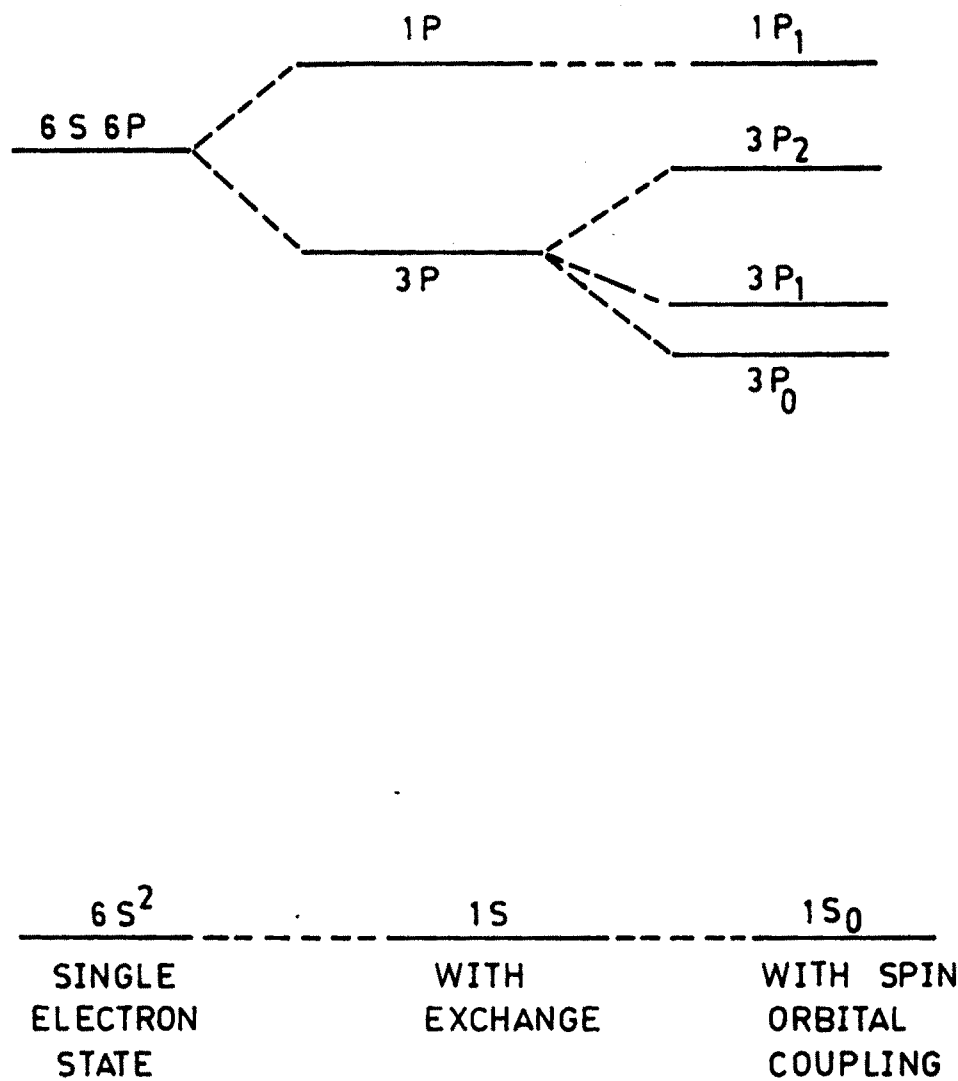


FIG. 5-1— ENERGY LEVELS OF THE FREE Bi^{3+} ION

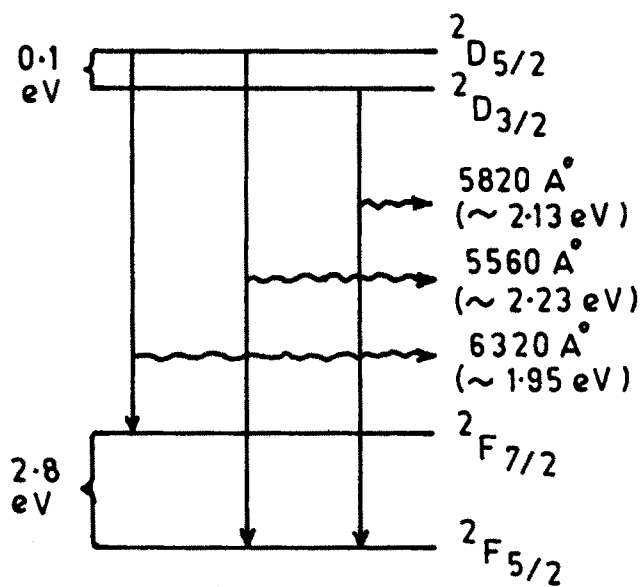


FIG. 5-2- ENERGY LEVEL DIAGRAM OF Ce^{+3} IN CaO .