

## **CHAPTER - V**

### **SUMMARY AND CONCLUSIONS**

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The studies on rare earth doped alkaline earth sulphate phosphors are discussed in the preceding chapters by considering behaviour of typical phosphor system  $\text{BaSO}_4$  : Dy co - doped by rare earth (Tb, Yb, Pr) and non - rare earth (Cu, Mn) co - activators. A charge compensator  $\text{Na}_2\text{SO}_4$  has been used to investigate the enhancement effects. An attempt has been made to reveal the role of activator, co-activator and charge compensator so as to investigate the ways and means to improve luminescence output of the phosphor system under study. The luminescence output of the phosphors is measured in terms of EL brightness at ambient applied A.C. voltages and frequencies. The probable mechanism underlying various processes are highlighted wherever possible.

#### 5.1 Preparation of Phosphors and Structural Studies :

Chapter II is totally devoted for various aspects of synthesis of phosphors (2.1) and method of preparation of  $\text{BaSO}_4$  phosphors (2.2). The main intention of present investigation is to improve the luminescence output of  $\text{BaSO}_4$  phosphor by suitably choosing activator, co - activator and to optimise their concentration. It was also intended to further improve

the luminescence output using suitable charge compensator. Keeping this view in mind, a series of BaSO<sub>4</sub> phosphors was prepared as per the table 2.2 (a) and 2.2 (b). The method of preparation is briefly indicated with the help of flow chart given in fig. 2.1.

On the basis of XRD studies an attempt has been made to reveal the crystallographic structure of phosphor system under study (chapter III). BaSO<sub>4</sub> basically belongs to orthorombic crystal system, with lattice constant  $a = 8.86$  A.U.,  $b = 5.4412$  A.U. and  $c = 7.1401$  A.U. The nature of XRD patterns shown in fig. 3.17, indicates that incorporation of activator, co-activator and charge compensator Na<sub>2</sub>SO<sub>4</sub> doesnot bring about any appreciable change. However, changes in the relative peak intensities are attributed to the enhancement effect due to charge compensator explained in terms of charge compensation theory. The results so obtained are consistent with the results obtained by other workers in case of CaSO<sub>4</sub> phosphor system.

## 5.2 Electrical Characterisation : -

Electrically BaSO<sub>4</sub> phosphor belongs to the category of insulator having resistivity of the order of  $10^8 \Omega$  cm. The resistivity of phosphors of ambient activator and co - activator concentration have been determined at various frequencies from I-V curves. These

curves obey ohmic law and has been reported graphically in fig. 3.10-14. The general observed trend is to decrease the resistivity with increase of frequency. This behaviour could be thought in terms of a parallel plate capacitor between which, our given phosphor system behaves as a dielectric medium. The capacitive reactance is inverse function of applied frequency. However, rapid decrease of resistivity in case of  $\text{Na}_2\text{SO}_4$  added phosphors is contemplated in terms of excess incorporation of activator and co-activator ions in the host lattice of  $\text{BaSO}_4$  on account of charge balancing. These studies also reveal that the present phosphor system accepts only a trace of co-activator in  $\text{BaSO}_4$  : Dy phosphor. Any higher concentration of co-activator instead of improving the quality of phosphor, deteriorates it.

5.3 EL studies of  $\text{BaSO}_4$  : Dy : Tb/ Yb/ Pr/ Mn/ Cu Phosphors and Their Voltage and Frequency Dependence : -

The intention of undertaking EL studies of  $\text{BaSO}_4$  : Dy : Tb, Yb, Pr, Mn, Cu phosphors is not to investigate the mechanism of EL process underlying the phosphor system of this kind. This is because some efforts have already gone by earlier workers,<sup>2,3</sup> in understanding the mechanism of EL process in case of alkline earth sulphate phosphor. According to them, the

possible steps involved in EL process are as follow :

- i) Excitation of Charge carriers by field ionisation of impurity ion electrons.
- ii) Acceleration of charge carriers by the action of electric field localized in narrow region.
- iii) Transport of energy to the radiating site by the movement of accelerated charge carriers.
- iv) Transfer of energy to radiating centre by capture of charge carriers.
- v) Emission of light by impurity state to impurity state transitions.

There is no reason to have any other EL mechanism than that mentioned above to exist in the present phosphor system.

Secondly in the present investigation, measurement of EL brightness is considered as a tool to investigate optimising conditions to improve luminescence efficiency of the phosphor system under study. It has been proved that EL brightness of the phosphor obey power law relation :

$$B = a V^n$$

with applied a.c. voltage. The existence of powerlaw relationship between brightness and voltage indicate the possibility of bimolecular recombination process with centres. It is also concluded that this powerlaw



relation exist between B and V irrespective of concentration of activator, co - activator and presence of charge compensator. In other words the said factors doesnot alter the basic mechanism of EL process underlying the phosphor system under study.

There are five types of co - activators used in the present phosphor system. Out of these three co - dopants viz. Tb, Yb and Pr belong to rare earth category and remaining two viz. Mn and Cu belong to non rare earth category. The results indicate that EL performance of rare earth co - doped phosphor is much better as compared to non-rare earth co - doped phosphor.

EL brightness is found to increase with increase of frequency of applied electric field. This phenomenon has been explained in terms of exposition of phosphor to peak value of applied field  $e$ , twice in a cycle.

#### 5.4 Enhancement Effect due to Co-activators

Out of five co - activators used, the performance of a trace amount of Tb (0.001 wt. % ) doped BaSO<sub>4</sub> : 0.075 wt. % Dy phosphor seems to be the highest as far as its EL brightness is concerned. This has been indicated in fig. 4.15 and discussed at length in section 4.3.3 Yb, Pr, Cu and Mn co-doped phosphors follow successively in decreasing order as for as their

EL brightnesses are concerned. Better performance of rare earth co-doped phosphor as compared to non-rare earth co-doped phosphor has been explained in terms of ionic radii in section 4.3.3

The enhancement effect of EL due to a trace of rare earth co-activators (Tb, Yb and Pr) could be explained on the basis of energy transfer from co-activator to activator. Various workers<sup>4,5,6</sup> have considered the effect of co-activator in the enhancement of luminescence output in different phosphor systems. They have proposed probable mechanism of energy transfer underlying the process. Fig. (5.1) gives energy level diagram of Dy<sup>3+</sup> and Tb<sup>3+</sup>. Awasthi and Thakar<sup>5</sup> have considered the enhancement effect of luminescence in CaS: Dy: Tb phosphors. They have considered the energy transfer from  $4F_{9/2}$  (which is manifold of Dy) to  $5D_4$  (which is manifold of Tb), when concentration of Dy is low as compared with concentration of Tb. However, when concentration of Dy is higher and concentration of Tb is in traces, the energy transfer is from  $5D_3$  (which is manifold of Tb) to  $4F_{9/2}$  (which is manifold of Dy). Guo<sup>6</sup> Chang-xin et.al. have proposed the energy transfer mechanism to explain enhancement of luminescence of RE<sup>3+</sup> in Y<sub>2</sub>O<sub>3</sub> phosphor by trace of Tb<sup>3+</sup>. They have rejected the probability of resonance energy transfer from Tb<sup>3+</sup> to RE<sup>3+</sup>. They have also rejected the possibility of reabsorption of light from Tb<sup>3+</sup> to RE<sup>3+</sup>. The possibility

of energy transfer due to hole migration also does not suit as per their results. According to them, energy transfer via excitons from  $Tb^{3+}$  to  $RE^{3+}$  seems to be a proper mechanism underlying the process. They have proposed the model of energy transfer as follows fig. (5.2).

The addition of  $Tb^{3+}$  ions produces isoelectronic traps. These isoelectronic traps would trap holes first (step 1) then attract electrons to form excitons which are bound to  $Tb^{3+}$ . These bound excitons could turn into free excitons (step 2) by thermal disturbance. The free exciton could be bound by  $RE^{3+}$  and when they recombine,  $RE^{3+}$  ions are excited and radiate light.

The model suggested by Guo Chang - xi et al seems to be more appealing and may be employed to the energy transfer from co-activator to activator in the EL process of present phosphor system under study. In the light of the said model we propose the energy transfer from  $Tb^{3+}$  to  $Dy^{3+}$  in  $BaSO_4 : Dy : Tb$  phosphors as follows:

- i) During excitation excitons are formed which are bound to  $Tb^{3+}$ .
- ii) The bound exciton get released from  $Tb^{3+}$  and acts as free exciton.
- iii) The free exciton gets bound to  $Dy^{3+}$ . This way



transport and transfer of energy takes place from  $Tb^{3+}$  to  $Dy^{3+}$ .

iv) This consequently excite  $Dy^{3+}$  which ultimately radiates characteristic emission. The confirmation of said mechanism however, needs some extensive spectroscopic studies.

Similar energy transfer takes place from  $Yb^{3+}$  to  $Dy^{3+}$  and  $Pr^{3+}$  to  $Dy^{3+}$ .

#### 5.5 Enhancement Effect due to Concentration Optimisation of Activator and Co-activator :

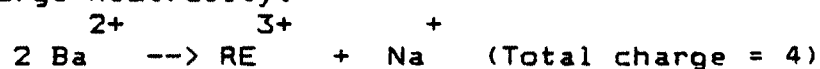
Various permutations and combinations of B-V curves for varied activator and Co-activator concentration have been depicted in figs. (4.16 - 4.20). These studies reveal that only a trace amount of co-activator ( 0.001 wt. % ) is sufficient for enhancement of EL brightness of  $BaSO_4 : Dy$  phosphor. Any excess co-activator concentration above the level of (0.001 wt. %) tends to deteriorate the EL brightness of  $BaSO_4 : Dy$  phosphor.

Secondly, it has been observed from the said plots that to have maximum EL brightness, an appropriate activator concentration of Dy is ( 0.075 wt. %). Any concentration below or above of this optimum value tends to harm EL brightness of  $BaSO_4 : Dy$  phosphor. The reduction of EL brightness due to

excessive concentration of activator and co-activator is explained in terms of concentration quenching which arises due to resonance transfer of energy from one activator atom to other, bringing in the possible migration of energy from one activator to other, which has more probability of getting dissipated without luminescence at quenching site.

### 5.6 Enhancement Effect due to Charge Compensator :

The charge compensator  $\text{Na}_2\text{SO}_4$  has pronounced effect on EL brightness of the phosphor system under study. This has dealt at length in 4.3.6. This enhancement effect is quite promising in case of rare earth co-doped phosphor such as Tb, Yb and Pr. An efficient phosphor viz.  $\text{BaSO}_4: 0.075 \text{ wt.}\% \text{ Dy}; 0.001 \text{ wt.}\% \text{ Tb}$  gets further enhanced in the presence of charge compensator  $\text{Na}_2\text{SO}_4$ . This effect has been explained on the basis of charge neutrality theory proposed by Kroger and Helingmann. This is indicated by following equation of charge neutrality.



However, this effect of enhancement is not observed in Mn and Cu co-doped phosphor. This has been indicated in fig ( 4.24 and 4.25 ) The probable reason for deterioration of EL output in case of  $\text{Na}_2\text{SO}_4$  added  $\text{BaSO}_4: \text{Dy}; \text{Mn/Cu}$  phosphor is the creation of charge imbalance produced due to  $\text{Mn}^{2+} / \text{Cu}^{2+}$  in the presence of

charge compensator ion Na<sup>+</sup>.

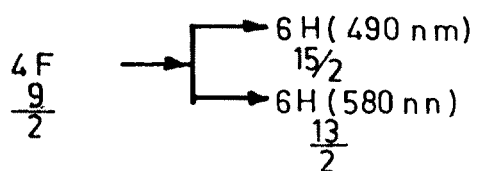
In brief out of number of phosphor prepared for present studies BaSO<sub>4</sub>: 0.075 wt.% Dy: 0.001 wt.% Tb with charge compensator Na<sub>2</sub>SO<sub>4</sub> seems to most efficient phosphor.

FIGURE CAPTIONS

Fig 5.1 Energy level diagram of Dy<sup>3+</sup> and Tb<sup>3+</sup> .

Fig 5.2 Schematic diagram of exciton energy transfer  
from Tb<sup>3+</sup> to Dy<sup>3+</sup> .

TRANSITIONS IN  $Dy^{3+}$



TRANSITIONS IN  $Tb^{3+}$

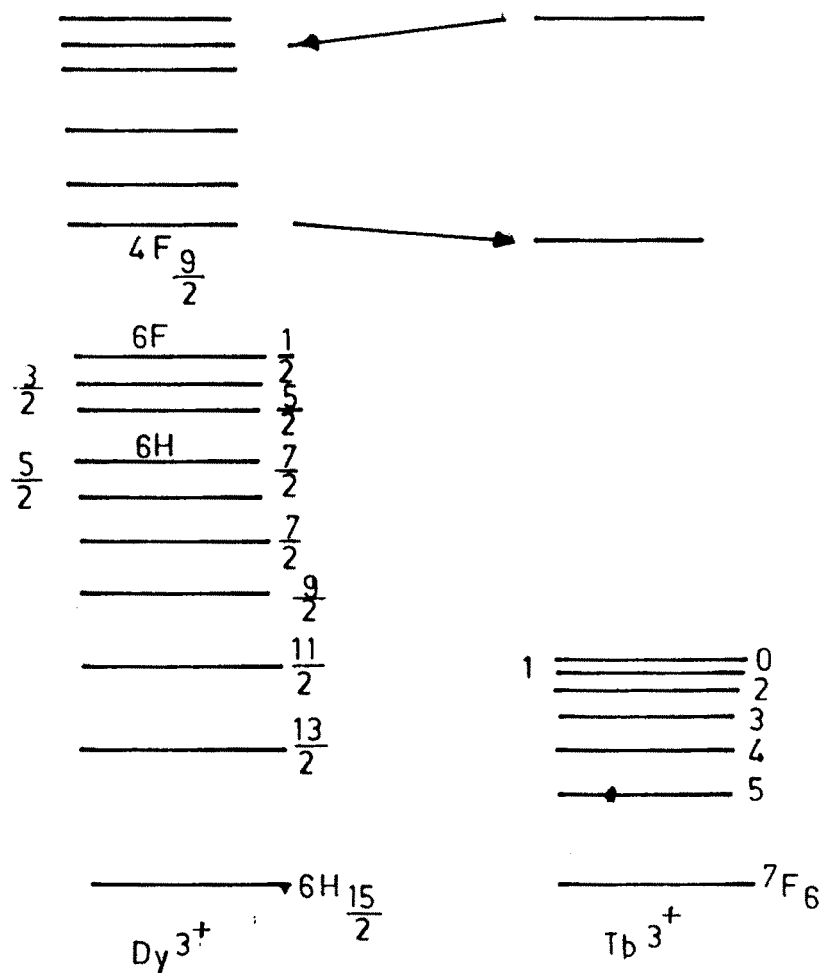
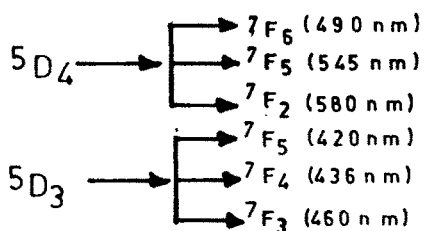


Fig. 5-1- Energy level diagram of  $Dy^{3+}$  &  $Tb^{3+}$

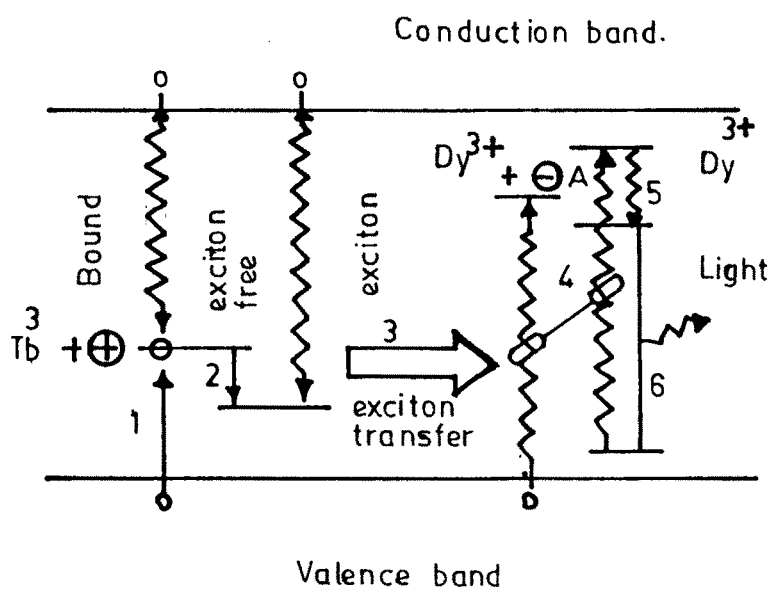


Fig. 5-2 Schematic diagram of exciton energy transfer from Tb<sup>3+</sup> to Dy<sup>3+</sup>

(⊕ and ⊙ represent holes, ⊖ and ● represent electrons)

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