

CHAPTER VII

RESULTS AND GENERAL DISCUSSION



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Photoluminescence, Thermoluminescence, Electroluminescence and thermally stimulated conductivity properties of doubly doped sulphide phosphor (cas) are discussed in earlier chapters. This study is basically aimed at finding the effect of first activator and second activator on the luminescence behaviour in general. Significant findings of these investigations are presented below and attempts have been made to correlate the results.

7.1 : Nature of decay :-

The analysis of phosphorescence decay curves is carried out to decide the mode of decay. The study of decay curves, plots of $\log I$ versus $\log t$ and $\log I$ versus t are almost (fig 3.7) linear. This suggests that decay may be hyperbolic or power law decay and can be represented by the equation of the form.

$I = I_0 t^{-b}$. where I is intensity at any time t and I_0 is the intensity at the start of decay and b is decay constant. For hyperbolic decay $b = -2$ and for power law decay $b = -1$. In the present investigation b is not exactly equal to unity, but it is around unity. This excludes the possibility of hyperbolic decay or power law decay. However decay can be explained on the basis of monomolecular superposition theory. According to this theory, such a decay is a resultant of superposition various exponentials corresponding to different traps. Thus the observed decay is combination of exponentials.

7.2 : ACTIVATION ENERGIES FROM DECAY CURVES :

For determination of activation energy in the present study each decay curve has been split into exponentials by peeling off procedure. Trap depths corresponding to these exponentials have been calculated. The trap depths are in the range of 0.67 eV to 1.36 eV for slowest exponential and for second exponential 0.66 eV. to 1.2 eV. (Ref. table 3.2). This indicates that variation of activation energy with concentration of Mn:Dy and Bi:Tb is marginal and unsystematic. This suggests that activators modify the relative importance of traps which are responsible for luminescence. 9

7.3 : DISTRIBUTION OF TRAPPING STATES :

In the present study the values of b are around unity, which suggest that distribution may be uniform. This conclusion is supported by plots between log I versus log t and log I Vs t. The nature of the graph is nearly a straight line. This indicates that distribution of traps may be uniform.

7.4 : GLOW CURVES :

The comparative study of thermoluminescence glow curves of CaS, (undoped) CaS : Mn : Dy and CaS : Bi : Tb. Glow peak temperature is around 433^oK for CaS undoped and glow peak is shifted to 613^oK which host is doped with (Mn:Dy) and (Bi:Tb). Addition of activators to the host nearly increases the efficiency of phosphors. This indicates that activators will modify the traps and relative importance (density) of the trap. The experiments carried out in the direction of optimum

concentrations reveal that CaS:Mn:Dy (Mn=0.1%, Dy = 0.001%) and CaS:Bi:Tb (Bi = 0.1%, Tb = 0.005%) give maximum TL output. Thermoluminescence glow curves of uv excited samples are shown in fig. (4.1 to 4.7 and 4.9, 4.10). As seen from fig. 4.1 to 4.7 that all the glow curves exhibit a single broad peak around 613^oK. from the shape of glow curve to seems that temperature slightly changes for some activator concentration. This indicates that phosphor may have another peak at slightly different temperature. These peaks might have been situated close to each other and their resultant is obtained as a composite glow curve. In the present study, however the isolated peaks are not resolved using partial bleaching technique. It is observed that overall shape of the glow curve is not significantly affected by variation of activator concentration (Mn:Dy, Bi:Tb). Only intensity changes with activator concentration.

7.5 : ACTIVATION ENERGIES FROM GLOW CURVES :

For uv-excited samples the activation energies are calculated by using methods due to 1) Urbach 2) Luschi 3) Halperin and Branner 4) Chen 5) Gross weiner. From the table 4.2, it is clear that activation energy does not vary much with activator concentration. The effective trap levels from CaS:Bi:Tb are between 0.44 ev to 1.2 ev and for CaS:Mn:Dy 0.5 ev to 1.4 ev. The observed variation is not systematic with respect concentration variation. This suggests that addition of activator (Mn:Dy, Bi:Tb) do not introduce new traps but only modify the relative importance of traps which are responsible ^{for} luminescence. The trapping

levels may not be associated with activator but they are likely to be due to the defects in the crystal structure.

7.6 : SIZE OF TRAP : (CAPTURE CROSS SECTION) :

The size of trap have been estimated from values of frequency factor. The size of trap is about 10^{-22} cm². Thus the trap in the present case may be regarded as medium size trap.

7.7 : DOSE DEPENDANCE :

The peak intensity is found to be a function of excitation dose. The peak intensity of a glow curve of uv-excited sample, initially increases gradually and then saturates around a uv excitation of 45 minutes. (Fig.4.11) A 5 minutes test dose of uv-excitation is found to be sufficient for good TL & put.

7.8 : EL. BRIGHTNESS - VOLTAGE DEPENDANCE :

The electroluminescence brightness is function of applied voltage. The threshold voltage decreases as frequency increases. When the voltage is increased beyond threshold it is found that the brightness increases enormously (fig. 5.6, 5.9) Thus steep increase in brightness with small increase in voltage is found to be ir-respective of activator concentration. This indicates that, activator concentration may not be playing important role.

It has been found that plots of log B Vs log v exhibits a linear relationship at lower frequency range and it becomes

non-linear at higher frequencies. This indicates that power law relation is obeyed at lower regions and then it will obey exponential relation. The power law relation $B = av^n$ holds good between brightness and voltage with in the voltage range under study. saturation of electroluminescence brightness is not observed. The existence of power law relation between B and V_a indicates the possibility of bimolecular process. In the recombination of electrons with recombination centres.

7.9 : BRIGHTNESS FREQUENCY DEPENDENCE :

It is found that brightness is function of frequency, applied voltage (a.c.). From the graph between log B versus log f (fig 5.22 and fig. 5.23), it is observed that at lower frequencies brightness increases almost linearly. The frequency range over which linear relationship holds good depends on the exciting voltage. At higher voltage and frequency, brightness increases more rapidly and it saturates. The observed behaviour is in accordance with equation given by Thornton and D. Curie -

$$B = B_0 \cdot \frac{n_0^2 \alpha}{(1 + n_0 \alpha / 2f)}$$

7.10 : EFFECT OF ADDITION OF ACTIVATORS ON EL-BEHAVIOUR :

In the present study it is found that for various samples with different activator concentrations of Mn:Dy and Bi:Tb, The nature of voltage and frequency dependence of brightness is almost similar. This indicates that activator do not significantly affect the EL-behaviour.

7.11 : BRIGHTNESS WAVES :

The brightness wave pattern for typical samples is as shown in fig. 5.24. It may be seen that the brightness wave exhibits single broad peak per cycle of the applied voltage. The brightness wave shows single peak it indicates that the electron traps are located close to luminescence centres.

7.12 : MECHANISM OF EL :

For EL emission comparatively high fields are required. For all samples the threshold voltage is found to be around 400 volts. Requirement of an intense electric field for EL emission along with power law relation between brightness and voltage suggests that the probable mechanism of EL is likely to be the direct field ionisation of either valence band electrons or impurity centres where the transfer of electrons takes place by quantum mechanical tunneling process. Further the activator concentration₂ variation₂ gives no significant change in brightness or threshold voltage. This leads to say that EL mechanism in the present phosphor (is) may be (mainly) due to the field ionisation of valence band electrons rather than due to impurity centres.

7.13 KINETICS OF LUMINESCENCE

The observed decay in phosphorescence studies can be explained on the basis of monomolecular superposition theory which indicates that kinetics involved in the luminescence process is likely to be monomolecular (First Order). From TL-studies the kinetics of luminescence can be determined by the symmetry factor. U_g is the characteristic of the type of kinetics involved in the process. 9

From the value of U_g it seems to be the monomolecular (Table No.4.2)

From EL-studies, the existence of power law relationship between brightness and voltage and variation of brightness with frequency as per equation given of D. Curie, suggests that the kinetics may be second order (bimolecular).

All the above said results go in favour of stating that CaS:Mn:Dy and CaS:Bi:Tb with charge. Compensation shows as a good luminescent materials in general exhibiting both TL and EL.

7.14 THERMALLY STIMULATED ELECTRICAL CONDUCTIVITY

The thermally stimulated conductivity is observed. In the present study large band gap for undoped phosphor are obtained. In both types of phosphors of composition CaS:Bi:Tb and CaS:Mn:Dy presence of activator (impurity) is found to decrease band gap. In CaS:Bi:Tb and CaS:Mn:Dy phosphors ' E_g ' is smaller than that of undoped CaS. Calcium sulphate with activator or (Bi:Tb) has the smallest value 1.666 eV.

Thermally stimulated conductivity measurements do not show much change, in the magnitude of conductivity with temperature and with addition of activators. Thus Mn:Dy and Bi:Tb does not affect the thermally stimulated conductivity.

Possibly this result can be correlated with the finding from thermoluminescence study that addition of activator only increases relative population in the host and do not give any new traps in the synthesis of phosphor. Study of these phenomenon under x-ray irradiation, monochromatic glow curve studies, emission spectra, extensive work on conductivity measurements remain the scope for further studies.