CHAPTER VII

RESULTS AND GENERAL DISCUSSION

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The Phosphorescence, thermoluminescence, electroluminescence and electrical conductivity measurments are carried out for the sulphate phosphors in present work. The investigations have brought out some significant results. The detailed results are given at the end of respective chapters. Some of the important results are discussed in this chapter and an attempt has been made to co-relate these results, which will help to understand optical and electrical properties of activated sulphate phosphors.

7.1 PHOTOLUMINESCENCE STUDY

7.1.1 NATURE OF DECAY

Study of phosphorescence decay reveals that, plots of log I vs log t are   linear. This suggests that decay may be hyperbolic or power law decay and can be represented by the equation of the form $I = I_o t^{-b}$

For hyprbolic decay b =2 and for power law decay b = 1. In the present study, observed values and calculated values of 'b', show a considerable departure from unity, (less than unity). This eliminates 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 resultant of superposition of various exponentials, corresponding to different traps. Further investigations are needed to confirm exact nature of trap distribution.

7.1.2 ACTIVATION ENERGIES FROM DECAY CURVES

To determine the activation energy, each decay curve is split

into exponentials by 'peeling off' procedure. Trap depths corresponding to these exponentials have been calculated. The values of trap depths are in the range of 0.59eV to 0.69eV for slowest exponential, 0.45eV to 0.56eV for Middle exponential, and 0.45eV to 0.46eV for fastest exponential (Table 3.2). This indicates that, shallow traps decay fast. The variation of activation energy with concentration of Mn and Eu is marginal and unsystematic. This is probably due to perturbation of trapping states This sugests that activators do not introduce new traps which are responsible for luminescence.

The trap depths are seen to have lower range than those obtained from thermoluminescence studies for the same sample. This may be due to the emptying of the shallow traps at room temperature at which PL is recorded-

7.1.3 TRAP DISTRIBUTION

The observed and calculated values of 'b' are less than unity, indicating slow decay. The straight line nature of graph log I Vs. log t is sugestive of uniform trap distribution. The observed and calculated values of b indicate that, trap distributin is non uniform, (b $<$ 1). As such distribution more probably is quasiuniform. Further investigations are needed to confirm exact nature of trap distribution.

7.2 THERMOLUMINESCENCE STUDY

7.2.1 T.L.GLOW CURVES

Comparative study of TL glow curves of undoped $CaSO_4$, $CaSO_4$: Mn, $CaSO_4$:Eu and $CaSO_4$:Mn:Eu clearly indicates that 140°c peak is basically the characteristic of the host $CaSO_4$. presence of Mn and

Eu mearly increase the efficiency of the phosphors, under uv excita-
tion as well as under gamma excitation. This indicates that activators
do not create new traps but increase the relative importance of the
traps . For typical concentration of Mn:Eu   second peak around
240°c is observed, even for low energy irradiatins like uv. For
such concentrations traps responsible for high temperature (240°c)
peaks are more populated.

The investigation carried out in the direction of optimum concen-
trations reveals that $CaSO_4$:Mn:Eu(Mn 0.1%, Eu 0.05%) gives maximum
TL output after uv excitation, while $CaSO_4$:Mn:Eu (Mn 0.1%, Eu 0.01%)
gives maximum TL output after gamma excitation.

TL glow curves of uv excited samples are shown in the fig.
4.6 to 4.10 .Overall   shape of glow curves remains same, though
the concentration of activator is changed. Only peak intensity changes
with concentration.

TL glow curves for gamma excited samples are shown in the
fig. 4.11 to 4.13. The glow curve exhibits single peak around 140°c,
indicating that similar traps are present, as that found after uv excita-
tion. The presence of single prominent peak indicates no possibility
of energy transfer.

7.2.2 ACTIVATION ENERGIES FROM GLOW CURVES

Activation energies for uv excited samples and gamma excited
samples are calculated by using various methods (table 4.5 - 4.7)
It is observed that, there is no significant variation in the activation
energy of uv as well as gamma excited samples. The activation energy
lies in the range of 0.6eV to 1eV.

Activation energy is also calculated for uv excited sample
using different rates of heating which lies in the range of 0.7eV
to 1.7ev. An attempt is made to find the activation energy by initial

rise method, which is found to be 0.66 eV.

It is revealed that addition of activators (Mn,Eu) do not creat any new traps but only modifies the relative importance of traps, responsible for luminescence. The trapping levels may not be associated with activator but they are likely to be due to the defects introduced during the formation of phosphors.

7.2.3 ESCAPE FREQUENCY FACTOR

The value of escape frequency factor 's' varyfrom 10^5 sec^{-1} to 10^{13} sec^{-1}, for uv excited samples and from 10^8 sec^{-1} to 10^{13} sec^{-1} for gamma excited samples (Table 4.5 - 4.7). However, no special significance could be attended to these findings.

7.2.4 SIZE OF TRAPS

The capture cross section(σ) is calculated from the value of escape frequency factor. The size of traps is in the range of 10^{-13} cm^2 to 10^{-21} cm^2 for uv excited samples and that of 10^{-13} cm^2 to 10^{-18} cm^2 for gamma irradiated samples. The traps in present investigation may be regarded as medium size traps.

7.2.5 DOSE DEPENDENCE

Peak intensity of TL glow curve is found to be a function of excitation dose. The peak intensity of a glow curve of uv excited sample, initially increases sublinearly and approaches to saturation for uv excitation of about 120 minutes.

While for gamma excited phosphor peak intensity of glow curve increases and reaches to a maximum value for 15 minutes of excitation and then decreases (fig. 4.18, 4.20).

7.3 ELECTROLUMINESCENCE STUDY

7.3.1 DEPENDENCE OF BRIGHTNESS ON VOLTAGE

The EL brightness is a function of applied voltage. The possible relationship between brightness and voltage is studied by plotting various graphs. From the graph of Brightness versus Voltage it is observed that, threshold voltage decreases, as frequency increases (fig. 5.1 to 5.3). It has been found that the plots of log B Vs. log V (fig.5.10 to 5.12) are linear over a wide range of voltage and show bending towards voltage axis at high voltages. The degree of linearity indicates the possibility of existance of power law relationship $B = aV^n$.

The bending of the log B Vs. log V plots, towards voltage axis is more probably due to the traps, not emptying as fast as they are filled at high voltages and giving rise to space charge scattering and hence increase in radiation less transitions at high field.

7.3.2 DEPENDENCE OF EL BRIGHTNESS ON FREQUENCY.

Brightness is also found to be a function of frequency of applied voltage. From the graph of log B Vs log f(fig.5.13 to 5.15), 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, brightness increases more rapaidly, than at lower voltages. At higher frequency, brightness increases slowly and finally it saturates. This can be understood on the basis of equation given by Curie as

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

At low frequency, the above equation attains the form, $B = B_o n_o f$, which explains the linear relationship.

At high frequency, the equation attains the form $B = B_o n_o^2$ which explains the saturation of EL brightness.

7.3.3 EFFECT OF ADDITION OF ACTIVATORS ON EL BRIGHTNESS

It has been observed that, for varous samples of different concentrations of Mn, Eu the nature of voltage and freqency dependance of brightness is almost similar. This indicates that, activators do not significantly affect the EL behaviour.

7.3.4 MECHANISM OF ELECTROLUMINESCENCE

In present study, the threshold voltage is found to be greater than 150 volts, ingeneral, indicating moderately high electric field for EL emission. The power law relation between brightness and voltage sugests that, the probable mechanism of EL in these phosphors is likely to be the direct field ionisation of either valence bandelectrons or impurity centres, where the transfer of electrons takes place by quantum mechanical tunneling process.

7.3.5 BRIGHTNESS WAVES

Fig. 5.16 shows typical brightness wave patternfor a typical sample. It is observed that brightness waves exhibit one peak per cycle of the applied voltage According to Waymouth and Bitter, the light emitting grains act as minute rectifying junctions.

In the present investigation, these spots themselves can be thought of as minute rectifying junction. The brightness waves do not show any secondary peaks. This indicates that the electron traps are located close to the luminescence centre. The nature of the peak observed is similar to sawtooth.

7.3.6 KINETICS OF LUMINESCENCE

The existence of power law relationship between the brightness and voltage indicates bimolecular process in recombination of electrons with luminescence centres. Also the variation of brightness with frequency is in accordance with equation (5.16) which points to the bimolecular process.

7.4 THERMALLY STIMULATD CONDUCTIVITY

$CaSO_4$ phosphors are reported to show thermally stimulated conductivity (TSC).This suggests the excitation of electrons (or holes) via conduction band (or valence band) favouring sub model II due to Halperin and Braner. The emission occurs by the liberation of electrons from elctron traps (or holes from hole trap) which correspond to the luminescence centre. The characteristic spectral emission suggests radiative transition between impurity state to impurity state.

In the present investigation it is observed that at room temperature phosphor behaves as insulator with large band gap as compared to semiconductor. Even at high temperature (225°c) the phosphor does not show any conductivity. But when the same phosphor is excited by uv it shows low conductivity around 210°c. This is thermally stimulated conductivity after excitation.

The band gap energy estimated by four-probe method does not agree with the reported band gap value for $CaSO_4$ .This may be due to limitations of temperature range of the instrument, in four probe set up. Suitable modifications in experimental set up are expected to give more satisfactory result.

7.5 COMPARATIVE RESULTS

TL study has brought that, first peak around 140°c is due to host. A second peak around 240°c is observed for certain cases,

with a range of optimum concntration of the doponts even for low energy radiation like uv.This suggests that second peak may be attributed due to the dopants for certain range of concentration.

The overall findings from comparative study of PL and TL are in agreement, showing that nature of traps involved in both are of similar origin and may be basically attributed to the host. Comparative study also brings out that, dopants and codopants do not contribute for creation of new traps, but only increase the population of the existing traps.From EL studies also it is found that, EL output is practically independent of activator concentration, This supports the results from PL and TL studies. The order of kinetics from EL studies and TL studies is bimolecular. Activation energies from PL studies are slightly lower (0.4 eV - 0.6 eV) as compared to these obtained (0.6 eV - 1.0 eV) from TL studies. This suggests a composite trap in which shallow traps get emptied at room temperature (PL) while deeper traps resulting into TL are released at higher temperature. Such a shallow medium and deeper trap distribution is also observed from "Peeling Off" Studies.

The appropriate phosphor synthesized with optimising parameter is $CasO_4 : Mn_{0.1} : Eu_{0.05}$ which is found to be basically an insulator. Under uv excitation, electrical conductivity though very low is observed.

Emission spectral studies, monochromatic glow curve analysis, further study of electroluminescence and of electrical conductivity with necessary modifications in instrumentation, along-with study over wider range of concentrations may help in understanding the phenomenon in better perspective and may give application orientation of such phosphors.