CHAPTER VII

RESULTS AND GENERAL
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7.1 Nature of decay :

Study of phosphorescence decay reveal that plots of log I versus log t are almost linear. This suggest 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 hyperbolic decay b = 2 and for power law decay b = 1. In the present study b is not exactly equal to unity, but it is close to 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 the superposition of various exponentials corresponding to different traps. Thus the observed decay is a combination of exponentials.

7.2 Activation energies from decay curves :

To find the activation energies, each decay curve has been splitted 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 0.53 eV to 0.57 eV for slowest exponential, 0.46 eV to 0.5 eV for second exponential and 0.42 eV to 0.44 eV for fastest exponentials (Ref. table 3.2). This indicates that shallow traps decay fast. The variation of activation energy with concentration of Mn and Sm is marginal and unsystematic.

This suggests that activators do not introduce new traps
but only modifies the relative importance of traps which
are responsible for luminescence.

7.3 Distribution of trapping states :

In the present case value of b is close to unity
which suggest that distribution may be uniform. This
conclusion is supported by the plot between I and t^{-1}.
This graph is a straight line, which indicates that
distribution of traps may be uniform. The above conclusion
is also supported by plot between I.t and log t. This graph
is approximately parallel to log t axis, which go in favour
of uniform trap distribution.

7.4 Glow curves :

Comparative study of TL glow curves of undoped CaS
CaS:Mn, CaS:Sm and CaS:Mn:Sm clearly indicate that 373°k
peak is basically the characteristic of the host CaS.
Presence of Mn or/and Sm mearly increase the efficiency of
phosphors. This indicates that activators does not create
new traps but increases the relative importance of the
trap. This sort of conclusion however can be supported by
emission spectral studies and monochromatic glow curve decay.

The experiments carried out in the direction of optimum
concentrations reveal that CaS:Mn:Sm (Mn:0.05% ,Sm:0.02%)
gives maximum TL output.

TL glow curves of uv excited samples are shown in fig.
4.7 - 4.13. As seen from fig. 4.7 - 4.13 that all the glow

curves exhibits a single broad peak around $393^{\circ}k$. From the shape of glow curves it seems that temperature slightely changes with concentration of activators (Mn and Sm). The shift in temperature indicates that instead of having a single peak around $393^{\circ}k$, the glow curve may have more than single peak. 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 activators (Mn, Sm). Only peak intensity changes with concentration.

TL glow curves for γ irradiated samples are shown in fig. 4.20 to 4.24. The glow curves were recorded 92 days after γ irradiation. All the glow curves exhibits two peaks, first around $423^{\circ}k$ (weak) and second around $475^{\circ}k$ (strong), peak around $393^{\circ}k$ observed in uv excited phosphors is missing which is probably due to room temperature decay of low temperature peaks. The high temperature peak which is not observed in uv excited samples may be probably due to high energy irradiation creating deep traps which favour high temperature peak. The observation however requires persual.

7.5   Activation energies from glow curves :

Activation energies for uv excited samples are calculated by using methods due to (i) Urbach (ii) Luschik (iii) Halperin and Braner   (iv) Chen (v) Grossweiner, (Table 4.2). From the table it is clear that activation energy does not vary much

with activator concentration. The effective trap levels are distributed from 0.4 eV to 0.9 eV. The observed variation is not systematic with respect to concentration variation. This suggests that addition of activators (Mn, Sm) do not introduce any new traps but only modifies the relative importance of traps which are responsible for luminescence. The trapping levels may not be associated with activators but they are likely to be due to the defects in the crystal strcture.

Activation energies for γ irradiated samples are calculated by Urbach formula (Table 4.4). Activation energy is almost constant with activator concentration variation.

7.6   Size of trap :

The capture cross section of effective traps have been estimated from values of fraqexx frequency factor. The size of trap is about 10^{-18} cm^2. Thus the traps 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. 4.18 to 4.19).

7.8   EL brightness-voltage dependance :

The EL brightness is a function of applied voltage. The threshold voltage decreases as feequency increases. It has been found that plots between log B and log V exhibits linear relationship over a wide range of voltage (fig. 5.7 to 5.11). This indicates that power law relation

$$B = aV^n$$

holds good between brightness and voltage.

7.9 Brightness-frequency dependance :

Brightness is also found to be a function of frequency of applied voltage. From the graphs between log B and log f (fig. 5.12 to 5.14), 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 rapidly that at lower voltages. At higher frequencies brightness increases slowly and finally it saturates. The observed behaviour is in accordance with equations given by Thornton and D.Curie.

7.10 Effect of addition of activators on EL behaviour :

It has been found that for various samples with different concentrations of Mn and Sm, the nature of voltage and frequency dependance of brightness is almost similar. This indicates that activators do not significantly affect the EL behaviour.

7.11 Mechanism of electroluminescence :

To observe EL emission comparatively high fields are required. For all samples the threshold voltage is found to be greater than 385 volts. This 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 in these phosphors is likely to be the direct field ionisation of either valence band electrons or impurity centers, where the transfer of electrons takes place by a quantum mechanical tunneling process.

7.12   Brightness waves :

Fig. 5.16, shows the brightness wave pattern for a
typical sample. It may be seen that the brightness waves
exhibits two peaks per cycle of the applied voltage.
According to Waymouth and Bitter the light emitting grains
acts as minute rectifying junctions. The excitation will
occure in some during one half of the cycle and in others
during next half cycle giving two peaks   in one complete
cycle. The observed peaks are not of equal amplitude. The
brightness waves do not snow the secondary peaks. This
indicates that the electron traps are located close to
luminescence centers.

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 first order (monomolecular).

From thermoluminescence studies plots of log I versus
t in isothermal decay are not straight line (fig.4.16) indica-
ting kinetics is not first order. However, plots of $1/\sqrt{I}$
versus time (in isothermal decay) are straight line (fig. 4.17)
which suggests that kinetics involved in luminescence process
may be second order (bimolecular).

From electroluminescence studies existance of power law
relationship between brightness and voltage and variation of
brightness with feequency as per equation given by D.Curie

suggests that kinetics may be second order (bimolecular). As such it seems that most probably the order of kinetics involved in luminescence process in general may be second order.

All the above said results go in favour of stating that CaS:Mn:Sm with charge compensation shows as a good luminescent material in general exhibiting both thermoluminescence and electroluminescence. 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.