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# CHAPTER VII

## GENERAL RESULTS AND DISCUSSION

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# C_H_A_P_T_E_R- VII

# GENERAL RESULTS AND DISCUSSION

This chapter is devoted to the results, their discussion and conclusions obtaindin the present investigations. Although some interpretations and inferences drawn from specific studies are described at the end of the preceding chapters, they are summarised and further tried for their corelation.

## 7. PHOSPHORESCENCE STUDY :

### 7.1.1 Nature of decay :

The first step to analyse the nature of decay is to find out whether it is exponential, hyperbolic or power law. This can be decided by observing straight line nature of the graphs between log (I) and (t), log (I) and log t respectively. In present case log I Vs log t plots are almost straight line implying the decay to be hyperbolic, which can be represented by equation of the type,

$$I = Io\ t^{-b} \quad ----- \quad (7.1)$$

Where 'I' is intensity at time 't' , $I_o$ is that at the start of the decay and b is decay constant. This hyperbolic decay is explained on the basis of Randall and Wilkins monomolecular theory, according to which such a hyperbolic decay is a result of superposition of various exponentials corresponding to different traps and can be represented by the equation

$$I = Io\ t^{-b} = I_{o1} \exp(-P_1 t) + I_{o2} \exp(-P_2 t) ----- + I_{on} \exp(-P_n t) --------- (7.2)$$

Where $I_{on}$ is phosphorescence intensity due to electrons in the traps of energy $E_n$ and $P_n$ is the transition probability of an electron escaping from a trap of depth $E_n$ and is given by

$$P_n = S \exp ( - E_n/KT ) \qquad \text{------} \ (7.3)$$

### 7.1.2 Activation energy from the decay curves :

Each decay curve has been split up into three exponentials and trap depths corresponding to these exponentials have been calculated by ' peeling off ' procedure. The value of E thus obtained for slowest ($E_1$) , middle ($E_2$) and fastest ($E_3$) exponentials vary from .57 to .62 eV, .50 to .52 eV, and .43 to .44 eV respectively ( table 3.2 ).

### 7.1.3 Distribution of trapping states :

It has been found that for all samples the value of b is close to unity, thus indicating that the trap distribution is likely to be quasi-uniform. The conclusion is supported by the plots between ( I.t ) vs log t. The curves are neither straight lines parallel to log t axis nor exponential as required by uniform and exponential trap distributions. In case of CaS:Sm:Nd, (I.t) increases, attains maximum value further decreases and finally becomes parallel to log t axis. While in case of CaS:Dy:Tb ( I.t ) decreases and becomes parallel to log t axis (fig.3.22 and 3.23 ). It may be concluded that the trap distribution responsible for phosphorescence decay is likely to be quasi-uniform.

### 7.1.4 Kinetics of PL :

The straight line nature of the plot of log I vs t represents first order kinetics and straight line nature of plot of $1/\sqrt{I}$ vs time represents second order kinetics. For second order and intermediate kinetics a straight line plot between log I vs log t assumes a slope equal to -2 and -1 respectively for $t \gg 1$. In present case plots are neither expontial ( fig. 3.13 to 3.18 ) nor hyperbolic ( fig. 3.19 , 3.20 ) and slope of log I vs log t $\neq 2$ . Decay law can however be represented by power law equation of the type $I = I_o t^{-b}$. Since 'b' is not exactly equal to unity but close to unity as required by intermediate process resulting from the traps of single depth, it excludes the probability [fig 3.22, 3.23 table (3.2)] of intermediate kinetics. On the other hand observed power law decay could be well explained on the basis of monomolecular superposition theory suggesting that kinetic involved in PL is likely to be monomolecular.

## 7.2 THERMOLUMINESCENCE STUDY :

### 7.2.1 TL glow curve :

a) Ultraviolet excited samples : For U.V. excited samples a single broad peak around temperature 105° c is observed for all CaS:Sm:Nd phosphors, whereas two broad peaks are observed first around 105°c and second around 190°c for all CaS:Dy:Tb phosphors. It is interesting to note that there is second prominent peak in in CaS:Dy:Tb as compared with that for CaS:Sm:Nd. The study of emission spectra may reveal the exactness of the above statement.

From the shape of glow curves it seems that the temperature of glow peak slightly changes with concentration of activators. The slight shift in temperature indicates that an apperent broad peak for all phosphors may be a composite peak having more than one peak which are situated closeby. The shape of the broad peak with slightly varing intensities inbetween also supports the composite nature of the glow peak. It is observed that over all shape of all the glow curves is not significantly affected by concentration of activators and second activators for all phosphors but peak intensity changes with concentration.[fig. (4.11, 4.12)].

b) $\gamma$ - irradiated samples : All the glow curves of gamma irradiated samples were recorded 92 days after irradiation. All the glow curves exhibit three peaks ( table 4.3 ), first around 155°c , second around 205°c and third around 260°c. The peak around 205° c is prominent for all prepared samples. Peak around 105°c observed in u.v.excited phosphors is found missing probably due to decay.

### 7.2.2 Activation energies from glow curves :

a) Ultraviolet excited samples : Activation energies E, of glow peaks were evaluated by several formulaegiven by i) Urbach (ii) Luschik (iii) Halperin and Branner (iv) Chen v) Gross Weiner ( table 4.4 , 4.5 ). However activation energies evaluated using Chen's formula are found to be higher as compared with others. An attempt is also made to estimate activation energy using initial rise method for a typical sample[fig.(4.13)].

Comparison of E values determined from thermoluminescence studies with those obtained from decay measurement carried out for the same samples indicates that energies corresponding to first glow peak are in close agreement with slowest exponential of decay. The E values coresponding to second glow peak being high,[table (4.6)] . This indicates that, to investigate deeper traps, one should adopt TL technique, rather than the decay.

b) Gamma irradiated samples : Activation energies from the glow curves for gamma irradiated phosphors are evaluated using Urbach formula table (4.7), for peaks arround 155°c, 205°c and 260°c. These activation energies are higher than those obtained for u.v. excited samples. This indicates that traps involved are deeper. It has been confirmed that gamma irradiation dose does not cause irradiation damage, Following procedure is used for this. After recording T.L. glow curve of gamma irradiated sample, the same sample was u.v. excited and its TL was recorded. The shape of glow curve, peak temperature and peak intensity remain practically unaffected as that for fresh sample, after u.v. excitation alone.

7.2.3 Escape frequency and size of traps :

a) After uv excitation : For CaS:Sm:Nd phosphor escape frequency factor was determined by using Randall and Wilkins formula and using energy evaluated by Urbach formula. The escape frequency factor lies between $1.28 \times 10^9$ $sec^{-1}$ and $1.68 \times 10^9$ $Sec^{-1}$ and size of the trap lies between $8 \times 10^{-17}$ and $1.5 \times 10^{-17}$ $cm^2$. Similarly for phosphors CaS:Dy:Tb for the first peak, frequency factor lies between $1.1 \times 10^{-18}$ and $9.7 \times 10^{-18}$ $cm^2$. For second peak, frequency factor lies between $1.2 \times 10^9$ and $5.08 \times 10^{10}$ and size of the trap lies between $8 \times 10^{-18}$ and $9 \times 10^{-18}$ $cm^2$ table (4.8).

b) After gamma irradiation : For all phosphors escape frequency factor lies between $8.2 \times 10^8$ and $2.9 \times 10^9$ $Sec^{-1}$ and corresponding size of trap lies between $5.4 \times 10^{-18}$ and $2.97 \times 10^{-17}$ $cm^2$ [table (4.17)].

### 7.2.4 Dose dependence study :

The intensity of glow peak is found to be a function of irradiation dose[fig. (4.15, 4.16)]. TL peak intensity is found to increase with dose. Saturation is around 45 minutes for the uv excited phosphors.

### 7.2.5. Kinetics of thermoluminescence :

The symmetry factor '$\mu g$' is a measure of the type of kinetics involved in the TL process. The values of $\mu g > e^{-1}$ ( table 4.4 , 4.5 , 4.6 ) suggest that possible kinetics is of second order. This statement is also supported by plot of '$1/\sqrt{I}$' versus 't' in isothermal decay, which is a straight line[fig. (4.14)]. This shows that kinetics involved in TL is of second order.

## 7.3 ELECTROLUMINESCENCE :

### 7.3.1 The voltage dependance of EL brightness :

The nature of possible relationship existing between brightness and applied voltage is examined by plotting log (B/V) vs (1/V) (ii) log (B/V) vs $(1/\sqrt{V})$ (iii) log (B) vs (V) (iv) log (B) vs (1/V) & (V) log (B) vs $(1/\sqrt{V})$. It is observed that none of these plots[fig. (5.2 - 5.6 )] show a definite linearity, indicating that the observed brightness voltage dependence is not exponential. However, the plots between log (B) vs log (V) [fig. (5.7 - 5.11)] show a linear relation with slight deviation at low and high voltage. The saturation of brightness takes place at higher voltages. Particularly for 1KHz, log (B) - log (V) linear relation holds good over wide range of voltages studied.

log (B) vs log (V) relation can be written as $B = aV^n$ . The valuesof n are listed in table (5.2).

There is no systematic change of threshold voltage at a given frequency for the phosphors of different concentrations.

### 7.3.2 Frequency dependance of EL brightness :

Brightness is also found to be a function of frequency of applied voltage. Typical graphs between log (B)-log (f) are shown in fig. ( 5.12 - 5.17 ). The results obtained can be summarised as (a) At low frequency brightness increased linearly (b) The frequency range over which the linear relationship holds, depends on the exciting voltage. At higher voltages brightness increases more rapidly than at lower voltages. (C) At moderately higher frequencies the brightness increases slowly and finally it saturates.

The sample KD 31[fig.(5.17)] does not behave as described above. Brightness decreases for higher frequencies. [Chapter I (51), (52)] .

### 7.3.3 Relative efficiency :

Fig. (5.18 a,b ) shows that brightness increases with supply energy and saturates, secondly with increase in energy (w) efficiency increases, reaches a maximum and further decreases.

### 7.3.4 Brightness Waves :

Photograph of brightness waves[fig. (5.19)] is presented for sample (KD30) at 2.2 KHz. It shows brightness waves having two peaks per cycle of applied voltage. These two peaks are not exactly symmetric in nature and have phase difference with applied voltage.

## 7.4 Thermally stimulated electrical conductivity of phosphors:

Measurement of conductivity for typical phosphors using four probe set-up reveals that as temperature increases conductivity initially decreases reaches minimum. This temperature is referred as invesion temperature (Ti). Beyond this temperature conductivity is found to increase. Such a phonomenon occurs in case of doped semiconductors at low temperature, where conduction is primarily due to extrinsic carriers. In fig (6.1, 6.2), region 'ab' is due to impurity carriers and in the region 'bc' current is carried by excited electrons in the conduction band (intrinsic region ). The values of conductivity corresponding to various temperatures are listed in table ( 6.1 , 6.2 ).

The values of band gap obtained are found to be 1.68 eV for CaS:Sm:Nd and 1.95 eV for CaS:Dy:Tb, for typical samples. These values are lower than the reported values of band gap of CaS.

The discipancy may be attributed to

i) Conductivity in the range of temp. 27°c to 250°c may be due to electrons at trapping sites.

ii) The formula and experimental set-up used in present work is for room temperature semiconductors. However here conductivity being thermally induced as such the formula needs due modification.

## 7.5 Correlation between PL , TL and EL :

The observations made in the study of TL, PL, EL lead to infer that the phosphors of composition $CaS:RE_1 : RE_2$ exhibit the above phenomenon to a good extent.

Presence of flux in the phosphor of composition $CaS:RE_1:RE_2$ enhance PL, TL and EL processes.

The corelation study of photoluminescence and thermoluminescence indicate presence of shallow and deeper traps. Population of shallow trap is comparatively more than the deep trap.

PL studies indicate that the kinetics is monomolecular as such shallow traps are nearer to the luminescent center. The nature of brightness waves in EL study is in favour with this conclusion.

The glow curves studies lead to second order kinetics. The straight line nature of graph between log B-log V leads to bimolecular process. The bimolecular process may thus be attributed to presence of deeper traps which are away from luminescence centre.

All the above obtained results lead to conclude that CaS:Dy:Tb with 0.0075 percent Dy and 0.05 percent Tb is a typical phosphor amongst those studied in present work. The phosphor of this composition exhibits Photoluminescence, Thermally stimulated luminescence and Electroluminescence to a good extent. Good Electroluminescence goes in favour of cubic structure of the phosphor, as revealed from XRD studies. Electrical conductivity measurements above inversion temperature have brought out the electrical behaviour of the sample studied. Study of above phenomena under X-irradiation, emission spectra, monochromatic glow curve studies are still left for a better understanding of these phosphors.

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