
CHAPTER VI

GENERAL DISCUSSION AND RESULTS

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The phosphorescence and thermoluminescence studies carried out for the phosphors prepared under appropriate conditions bring out salient features mentioned below :

PHOTOLUMINESCENCE STUDY :6-1 Nature of Decay :

Measurements of phosphorescence decay reveal that the plots of logarithm of intensity (I) versus log t are almost linear. This suggests that the decay is hyperbolic and can be represented by the equation of the type

$$I = I_0 t^{-b}$$

where I is the intensity at time t, I_0 at the start of decay and b the decay constant.

This hyperbolic decay is explained on the basis of Randall and Wilkins monomolecular theory. According to this theory, such a hyperbolic decay is a result of the superposition of various exponentials corresponding to different traps. This can be expressed by the equation :

$$I = I_0 \exp. (- P_1 t) + I_{02} \exp. (- P_2 t) + \dots \dots \dots I_{0n} \exp. (- P_n t)$$

Where I_{0n} is the phosphorescence intensity due to electrons in the trap of energy E_n and P_n is the transition probability of an electron escaping from a trap of depth E_n .

6-2 Activation Energies from Decay Curves :

Each decay curve has been splitted into three exponentials by the 'peeling off' procedure. Trap depths corresponding to these exponentials have been calculated which are found in good agreement with those obtained from T.L. glow curve studies.

The value of E is found to vary from 0.24 eV to 0.55 eV for slowest exponential and 0.20 eV to 0.42 eV for fastest exponential (Ref. table 4.2). This supports the use of Randall and Wilkins monomolecular superposition theory.

what do you mean by good agreement? How the slowest & fastest are affected by the peaks.

6-3 Distribution of trapping states :

The distribution of trapping states is ascertained by using the relation,

$$I = \frac{NkT}{t} \left[1 - \exp(-st) \right]$$

for uniform trap distribution the above equation takes the form.

$$I = I_0 t^{-b}$$

In the present work the value of 'b' is neither unity nor close to unity which rules out the possibility of uniform or quasiuniform trap distribution. However, the value of 'b' for all the samples fluctuates between 0.18 to 0.55 indicating thereby that the trap distribution is likely to be non-uniform.

Above conclusion is supported by a plot between I.t and log t obtained for these samples (fig. 4.16). The curves are neither straight lines parallel to log t axis nor exponential as required by uniform and exponential trap distribution respectively. They are found to be increasing ones, suggesting

that the trap distribution is non-uniform. The curves also give an idea about the density of traps at various depths contributing to the phosphorescence decay.

It is observed that addition of Bi and Mg seems to influence the distribution of trap densities.

6-4 Thermoluminescence Study :

6-4.1 T.L.glow curves :

a) Gamma irradiated samples :

All the glow curves of gamma irradiated samples were recorded 45 days after irradiation. Glow Peak temperatures for all the samples are around 200°C (ref. table 5.1). It is observed that the peak positions and the general shape of the glow curves are affected by the addition of activator (Bi) and coactivator (Mg).

b) Ultraviolet irradiated samples :

For all the ultraviolet irradiated samples, the first peak is around 100°C . However samples V_4 , V_5 , V_9 , V_{11} , V_{12} , V_{13} , and V_{15} show second peak around 200°C . Maximum intensity is recorded for V_{14} sample (Ref. table 5.2),

The peak around 100°C would have got probably recorded for gamma irradiated sample if glow curves were recorded immediately after irradiation. But due to the lapse of time between irradiation and recording of the glow curve, peak around 100°C seem to have decayed and hence the only peak around 200°C which is more stable is observed. Thus the peak around 200°C is not a single peak but is probably the composition of number of peaks situated around 200°C .

6-4.2 Activation Energies from glow curves :

a) Gamma irradiated samples :

Activation energies from the glow curves are calculated using various formulae mentioned in chapter-5. The values of activation energies calculated using these formulae are found to be consistent (Ref. Table 5.3 to 5.6).

A comparison of E values determined from thermoluminescence study with those obtained from decay measurements carried out for the same samples indicates that the energies corresponding to the glow peak are in close agreement with slowest exponential of decay.

b) Ultraviolet irradiated samples :

A comparison of E values for above from thermoluminescence study with those obtained from measurement of decay indicate that the energies corresponding to the glow peak are in close agreement with the fastest exponential of decay.

6-4.3 Variation of activation energy with activator and coactivator concentration :

a) Gamma irradiated Samples :

It is observed that activation energy does not vary significantly with the addition of activator as well as coactivator. They vary from 0.17 eV to 0.99 eV (table no. 5.3 and 5.4) This indicates that addition of activator or co-activator only modifies the relative importance of traps, responsible for thermoluminescence but not the mean depth.

Centres
at
near
0.17 to 0.99
is a very
large
range
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out

b) Ultraviolet irradiated samples :

It can be seen from tables 5.5 and 5.6 that activation energies vary from 0.17 eV to 0.78 eV for the first peak and 0.37 to 1.12 eV for second peak. The addition of Bi or Mg do not introduce any new traps. The variation is shown in fig. 5.20 and 5.21.

6-4.4 Escape frequency factor and size of the traps :

It is observed that for both the excitation sources, the value of S obtained vary from 10^2 to 10^{13} sec^{-1} . The value of S is evaluated using Randall and Wilkins formula, The value of E obtained from Halperin & Branner's formulae were used to obtain the value of S . The size of the traps vary from 10^{-13} cm^2 to 10^{-24} cm^2 (table 5.7)

6-4.5 Dose Dependence Study :

TL.Glow curves plotted in the temperature range from room temperature and 300°C for U.V. irradiated phosphors reveal that saturation dose is around 75 minutes for the germicidal lamp (15 w) used. (fig. 5.17 to 5.18).

6-5 Nature and Origin of Traps :

It seems that incorporation of activator (Bi) or co-activator (Mg) into the host lattice does not give rise to new glow peaks in the temperature range studied. This indicates that the trapping levels may not be associated with activator or coactivator but they are likely due to the defect states in the host lattice.

The defects present in CaS may be either vacancies (cation or anion) or interstitials. However, from the consideration of atomic size (ionic radii of $\text{Ca}^{2+} = 0.99^\circ\text{A}$, $\text{S}^{2-} = 1.84^\circ\text{A}$

This is an initial basis.

and interstitial radius of CaS = 0.61 \AA), one can say that sulphur is too large to be accommodated in an interstitial site. Similarly the calcium ion interstitial seems to be very much unlikely. The possibility left is that of the defects arising due to calcium or sulphur ion vacancies. The earlier studies reported on CaS phosphors indicate that the sulphurisation of phosphor causes a reduction in trapping levels. Thus, the trapping levels in the present phosphor system may be attributed to the S vacancies. Such vacancies have been observed by Ghosh and Shankar in the EPR studies on polycrystalline CaS. According to them, there exist two types of vacancies : one is a single vacancy, -S ion vacancy surrounded by six Ca ions as its nearest neighbours and other is a divacancy - S ion vacancy having one Ca ion vacancy as one of the nearest neighbours.

During excitation, electrons from lattice are excited to these defects and are captured which in turn give luminous emission. However, from the present measurements it is not possible to attribute a particular vacancy to a particular glow peak. Trapping states in these phosphors exist prior to irradiation and these might have ^{been} created during the synthesis of phosphor at high temperature. Confirmation of this aspect requires further investigations.

6-6 Kinetics of Luminescence :

The symmetry factor $\mu_g = \delta/w$ is a characteristic of the type of kinetics involved. Calculations of μ_g suggest that possible mode of kinetics is of the second order. (Table 5.3 to 5.4). However the magnitudes of trap depth point towards the closer traps. Hence possible mode of kinetics may be

monomolecular or intermediate. Hence S values seem to be of lower magnitude. The monomolecular kinetics as indicated by Photoluminescence study and second order kinetic as pointed by T.L. studies needs further investigations.

The possibility of energy transfer in the present phosphor as is indicated by other workers can bring out usefulness of phosphor prepared. However, this sort of studies could not be carried out.

Resolution of a composite peak by partial bleaching technique could not be undertaken due to the limitations of the apparatus. Such a study can reveal the exact number of glow peaks and different traps involved in the process.

The comparative study of TL glow curves for CaS, CaS:Mg CaS:Bi, and CaS:Bi:Mg indicates that addition of Bi as an activator in the host increases the TL out put to a good extent. This result is in agreement with that of the earlier workers. Addition of Mg in the host increases TL out put to an extent. However CaS:Bi in presence of Mg as coactivator does not increase the TL output. But on the other hand decreases to a great extent. This indicates that Mg does not seem to be a good coactivator but may be helping in creating new traps. This requires further confirmation.