CHAPTER VI

DISCUSSIONS AND CONCLUSIONS
6.1 INTRODUCTION:

The main object of the present investigation is to know in what ways the traps and the centers in CaS: Ce phosphors are affected by the addition of another rare-earth impurity as Didymium. Therefore, the phosphorescence decay, thermoluminescence and emission spectral studies were carried out at room temperature. In the present chapter an attempt has been made to discuss and interpret the results obtained from aforesaid studies in the light of existing theories of luminescence.

6.2 DECAY STUDIES:

Most of the theories concerning the processes of phosphorescence decay and thermoluminescence start with the idea of emptying of the traps. According to Randall and Wilkins (1) the electrons have a Maxwellian distribution in the traps and the probability of release of an electron per second from the trap of
depth (E) at temperature (T) is given by

\[ P = S \exp \left( -\frac{E}{kT} \right) \]  \hspace{1cm} (6.1)

where \( S \) is a frequency factor and \( k \) is the Boltzmann constant. Though an attempt has been made by some workers\(^2\),\(^3\) to verify the above equation directly, it has not been yet possible to do so in the present phosphor system due to the limited nature of the study. However, a close correlation between the values of trap depths obtained from the decay and thermoluminescence studies justifies its validity. In the present studies the value of \( S \), as reported by Randall and Wilkins (1) for alkaline earth sulphide phosphors, \( 10^9 \) sec\(^{-1}\), is used throughout.

(A) **Decay Curves:** The phosphorescence decay is generally a first order or second order kinetics depending upon the relative location of traps and luminescence centers. It is observed that the decay is rapid during the initial stages and becomes slow during the later stages. This nature of decay curves can be explained on the basis of that the intensity of emission at any time depends on the probability of escape of electrons from the traps (1,4). In the decay curve the phosphorescence emission is due to the contribution of electrons at initial stages mainly from shallower traps and at later stages deeper traps become prominent.

In the case of localized centers the luminescence processes may be confined to within the centers and hence first order kinetics may follow, which has an exponential shape, the form being determined by the life time of excited state in the center and given by -
\[ I = I_o \exp \left( -\alpha t \right) \] \hspace{1cm} (6.2)

The second order kinetics involves a power law decay of long duration phosphorescence in which traps always play a fundamental role. This type of phosphors shows appreciable photoconductivity and is represented by

\[ I = I_o t^{-2} \] \hspace{1cm} (6.3)

If the decay is of the first order, a straight line relation comes out corresponding to eqn. (6.2), when log of intensity is plotted against time. Whereas in the second order process, the reciprocal of square root of the intensity if plotted against time shows the straight line relation and further, a plot of log \( I \) versus log \( t \) should assume a value of \(-2\) at large values of \( t \). In the present study the two series of phosphors do not conform to any of the simple functional forms represented by equations (6.2) and (6.3), so these equations cannot be used to infer the specific mechanism or the process involved. The decay curves are found to be hyperbolic since the log-log plots are nearly straight lines for the time of observations, as shown in fig.3.7 Chapter III. Therefore, a power law relation is applicable of the form

\[ I = I_o t^{-b} \] \hspace{1cm} (6.4)

where \( b \) is the decay constant which decreases with increase in temperature (5). The value of \( b \) was estimated as described in Chapter III, in Table No. 3.1 and 3.2. The value obtained varied from 0.50 to 0.71. The deviation of this constant from
unity excludes the possibility of uniform distribution of trapping states. The value of correlation coefficient \(-r\) is very close to unity which suggests that there is a linear relation between \(\log I\) and \(\log t\).

The phosphorescence decay of some phosphors at room has been observed in one stage (6), in some phosphors in two stages (7) or even more (8), all the stages being exponential in nature (8). These different components of the decay may be ascribed to traps. When traps of different depths are present and each decays exponentially, then the hyperbolic decay is due to superposition of exponentials arising from the decay of traps of different depths (2,9). As the number of exponentials increases the decay curve changes from a straight line to a hyperbolic curve on a semilog plot. The minimum number of exponentials required to form a hyperbolic curve is three (3,10). The hyperbolic decay of phosphor containing traps of different energies and populations can be explained by monomolecular superposition theory (4). As each group gives its own exponential component, the resultant phosphorescence intensity may be represented by:

\[
I_t = I_1 \exp(-p_1 t) + I_2 \exp(-p_2 t) + \ldots + I_n \exp(-p_n t).
\]

\[\text{(6.5)}\]

where \(I_n\) is the phosphorescence intensity due to electrons in traps of energy \(E_n\) so that

\[
p_n = S \exp\left(-\frac{E_n}{kT}\right)
\]

\[\text{(6.6)}\]

In the present case, the decay curves when analysed in the light of above method, give three exponentials. The exponentials were separated by the method of "peeling-off" of the
decay curve (3, 11, 12). It may not be justifiable to conclude, because of the limitations of the method, that they refer to the total number of exponentials involved in the decay of these phosphors. However, the success of this method is quite satisfactory. From the slope of these exponentials the trap depths were calculated as described in Chapter III in Table No. 3.1 and 3.2.

(B) Variation of decay constant with time: The decay constants were calculated at 15, 20, ...... secs, etc. after the cessation of excitation and graphs were plotted between decay constant Vs. time as shown in fig. 3.8 in Chapter III. As seen from the graphs, the decay constant slightly increases with time. This may be explained on the basis that the overall decay constant associated with different group of traps varies during the decay period as the shallower traps contribute to the initial stages of decay, whereas deeper traps contribute only after a sufficiently long time has elapsed. It may be concluded that larger value of 'b' corresponds to deeper traps.

(C) Variation of decay constant with activator concentration: The variation of decay constant with activator concentration has been observed by many workers (8, 13) and it has been found to increase (14) or decrease (15) with the activator concentration. In the present case as seen from the graphs in fig. 3.9 (A - B) in Chapter III, the decay constant shows an overall increasing tendency with increase of Di concentrations and a decreasing tendency with increase of Cc concentrations. The increase in decay constant with increase of Di content has been reported by many
workers (16,17). The variation of decay constant is not much. The overall variation is 21% in DA-Series and 21% in DB-Series.

(D) Variation of trap depth with activator concentration: The values of trap depths obtained show no significant variation with activator concentration as shown in fig. 3.10 (A−B) in Ch.III.

Thus it appears that activator concentration only modifies the relative importance of some group of the traps without changing their meandepth. The results are further corroborated by thermoluminescence studies.

6.3 THERMOLUMINESCENCE STUDIES:

The most widely used method for determining the depth of electron traps in powdered phosphors is based on thermal de-excitation. The advantage of this method lies in the fact that it gives directly qualitative information about the trap distribution. However, this method has some basic limitations in that it can not reveal—

(a) the deep traps whose maximum glow lies in the range of temperature quenching.
(b) the traps which are very close and overlap.
(c) the magnitude of trapping and
(d) the exact value of 'S' (frequency factor) of the system under study.

This method is also affected by the heating rate and the kinetics of recombination of electrons with traps and centers. Despite all these limitations, the glow curve method remains one of the powerful tools in phosphor research.
(A) The Glow Curves: Glow curves for all the phosphors were obtained at three different uniform warming rates. The lower warming rate was aimed at achieving resolution of component peak. But this does not show any resolution and the intensity of thermoluminescence emission is very weak. It is found that there is no appreciable change in the general shape of the glow curves obtained at three heating rates except that the glow curves are comparatively less diffuse at higher heating rate. Glow curves of some representative phosphors are shown in fig. 4.4 (A-H) in Chapter IV. Generally glow curve for all the samples exhibit two peaks; however, only at higher concentrations of Cerium and at lower concentrations of Didymium one peak is observed with a shoulder. Two peaks in the case of CaS:Ce & CaS:Di,Zr have already been observed by some workers (16,18) in this laboratory. Glow curves are not very sharp which indicates that traps have a distribution in depth.

Since the phosphors used in the present investigation are in the powder form and not closely packed, it is difficult to draw any definite conclusions from these observations.

(B) Evaluation of Traps: A survey of various methods used for estimation of trap depths from glow curves has already been described in Chapter IV. In the present case the trap depths were calculated with the help of the Curie formula, i.e.

\[ E(eV) = \frac{T_g(0K) - T_g(\beta/S)}{\theta(\beta/S)} \]  

\[ ........... (6.7) \]

This formula gave a fairly consistent value of trap depth within the experimental error for three heating rates. This formula also
holds good at relatively lower warming rates which have been used in the present study.

The choice of the formula is based on the following reasons:–

The Randall and Wilkin's formula is an approximate one, the factor \( f(S, \beta) \) i.e. 0.1 is neglected. This formula gives slightly lower value of trap depth than the curie formula.

Urbach's formula is also an approximate one since it gives the trap depth value of right order at higher heating rates. But higher heating rates have not been used in order to get good resolution of different glow peaks.

The disadvantage of Garlick and Gibson's formula is that it does not make use of the data near the peaks but derives the trap energy from the wings of the peak.

An unsatisfactory value of \( E \) is obtained using Grossweiner's formula, since this formula is very much dependent on the shape of glow curve rather than peak temperature.

In Halperin and Brander's formula, the symmetry of the glow curve has been used. Since the glow curves are complex, a little change in shape may affect the trap depth value considerably. The consistent value of trap depths are not obtained by Booth's and Keating's method because they depend on peak temperature and symmetry of glow peak respectively.

(C) The variation of trap depth with activator concentration:

The values of trap depths estimated are given in Table No. 4.1 and 4.2 in Chapter IV. It is seen that there is no
regular variation of trap depth with change in activator concentration, suggesting that the activator does not introduce any new levels in the region studied. However the possibility of introducing very shallow or very deep traps still remains.

(D) Correlation of trap depth obtained from Decay and Thermoluminescence Studies: In the decay studies the trap depths have been calculated by 'peeling-off' of the decay curves. The average trap depth values corresponding to slow, middle and fast components are 0.68, 0.62 and 0.58 respectively.

In the case of thermoluminescence two peaks are generally observed as shown in fig. 4.5 (A – B) in Chapter IV. The corresponding average trap depth values are 0.68 and 0.74 respectively.

The value of trap depth (0.68 eV) is in agreement with the value of trap depth (0.68 eV) calculated from the slowest exponential of the decay curve. But the value of the other trap depth (0.74 eV) is found to be higher than the three trap depth values obtained in the decay studies. This is expected as in the thermoluminescence the phosphors are allowed to decay to a very low intensity, resulting in emptying of shallower traps, before the heating was started. Thus, only the deep traps which are not emptied in decay are emptied due to the thermal energy supplied.

In both the studies the trap depth values do not show any appreciable change with activator concentrations. These values are generally assumed to represent a group of traps having
a Gaussian distribution (9). The trap depths calculated from
the slowest exponential from the phosphorescence decay may be
assigned a value of trap depth corresponding to its maximum.
Such values are tabulated in Table No. 5.1 along with the average
trap depth calculated from the glow curves. The agreement between
the trap depth calculated from glow experiment and the peeling-
off of the decay curves justify the assumptions involved in the
theory, that is, the kinetics is monomolecular and that only one
groups of traps, whose experimental resolution has not been
possible to achieve here, is effective at the temperature of
study. The observed form of the decay is then due to the super-
position of intensities.

(E) Retrapping: The shape of glow curve depend on the
number of traps initially filled during excitation. When the
deeper traps are not filled due to excitation intensities or low
excitation time, variation in glow curves can takes place due to
retrapping of electrons by deeper traps freed from shallower
traps. Garlick (19) has pointed out that weak excitation is
one of the conditions for retrapping. In the present study, the
initial conditions were such as to ensure saturation of traps and
hence it may be assumed that retrapping was negligible. Our
experimental results of decay and thermoluminescence studies
are quite well explained by the simple theory of Randall and
Wilkins which neglects retrapping, justifying the assumption in
the theory i.e. the kinetics is monomolecular and that only one
group of trap is effective at the temperature of study. Shallow &
deep traps may be possible which are not effective at this tempera-
ture range.
<table>
<thead>
<tr>
<th>S. No.</th>
<th>Sample No.</th>
<th>DA- Series Trap depth(eV) as calculated from glow curves.</th>
<th>Trap depth(eV) as calculated from decay curves.</th>
<th>DB- Series Trap depth(eV) as calculated from glow curves.</th>
<th>Trap depth(eV) as calculated from decay curves.</th>
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<td>0.69</td>
<td>DB-17</td>
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</table>
(F) **Nature of Traps**: The energy storage in phosphors has been well ascribed to traps, but the origin of these traps is not fully understood. Depending on the origin, traps may be classified as (20):

(i) **Trap associated with specific impurity**: Certain impurities such as activator, co-activator, etc. have been found to act as traps in phosphors (21,22) and in some cases the trapping process involves change in the effective valence state of the activator ions (23).

(ii) **Trap associated with host crystal defects and other perturbations**: This is due to the formation of a region in the host crystal surrounding the defects with the effective excess of positive or negative charge relative to the normal crystal lattice and capture of electrons or holes there (24,25).

Levsin and Faizi (26) who studied CaS activated with various activators have reported that the trap group of depth 0.68 is present only in phosphors with Bi is one of the activator. But Curie (9) observed that the trap group is independent of activator concentration. Bube (20) in the case of ZnS has concluded that a trap may be due to defect in the lattice other than activator atoms and upto some extent activator may change the relative distribution of traps. In the case of CaF$_2$ activated with different rare earth, Adler (26) has concluded that the glow curve is determine by the activator, but the properties of the traps arise from the matrix. Investigations in our laboratory
with CaS as host material and different fluxes and activators, have revealed that the group of traps lying between 0.60 to 0.80 eV is effective in all cases irrespective of fluxes and activators (27-29). This gives support to the results obtained in the present investigation that groups of traps studied in the present phosphor system are not due to the activators, but to the host lattice itself.

6.4 EMISSION SPECTRA :

The spectral studies of the present phosphor system were carried out so that the location of peak emission may further help in getting information regarding the effect of activator concentration on the luminescence mechanism. The emission spectra of CaS:Ce;Di phosphors in general consists of two parts:

(i) Double band emission peaking at around green (5125 Å) and second at around yellow (5775 Å) characteristic of the CaS:Ce phosphor.

(ii) Three groups of lines in the orange-red region lying in the range 5600 to 6500 Å, characteristic of the CaS;Di phosphor.

(A) Band Emission : The bands are attributed to the luminescence transitions in the centers produced by the presence of Ce in CaS. The two band emissions from a number of substances containing Cerium are generally obtained by various workers (19, 30-33). Cerium differs from the other rare earth metals in so far as its trivalent ion contains only a single electron in the 4f shell, with the result that it gives band spectra rather than line. The transitions are attributed from the 2D excited state to the ground levels $^2F_{5/2}$ and $^2F_{7/2}$ in Ce$^{3+}$. Gobrecht (21) has ascribed
them to transitions from the excited state to the doublet level of the ground state. Ginther (30) and Leech (34), however, reported a double band peaking at 3200 Å and 3400 Å for CaF:Ce. The observed double band for CaS:Ce; Di may be attributed to the transition from $^2D$ excited state to the ground levels $^2F_{5/2}$ and $^2F_{7/2}$ of Ce$^{3+}$ in CaS. The difference in position in the double band may be due to the different media, CaF and CaS, in the two cases or it may even be due to different excitation levels of the luminescence center that originate the double bands. The difference between the energies of the levels $^2F_{5/2}$ and $^2F_{7/2}$ i.e. the difference of energy in ev of emission peaks at 5125 Å (2.407 ev) and 5775 Å (2.134 ev) is 0.27 ev. Similar difference calculated from the double band data of CaF, Ce phosphors reported by Ginther (30) and Leech (34) is 0.23 ev, which is of the order obtained for CaS:Ce phosphors. Corresponding difference in ev for double band emissions of Ce$^{3+}$ in Ce-sulphate (35) and Ce$^{3+}$ free ion (36) are 0.27 ev & 0.28 ev respectively.

(B) Line Spectra : In common with the other rare earth elements, the line like spectra in the present case is due to the incorporation of Di in CaS. The rare earth elements have different number of electrons in the 4f incomplete shell and shielded by (5s$^2$ 5p$^6$) octet. The different orientations of the spin ($S$) and orbital moment ($L$) vectors of the 4f electrons give rise to several quantum states, transitions among which result in fairly sharp lines. There sharpness is attributed to the fact that 4f electron are shielded from the external perturbation by the screening action of the (5s$^2$ 5p$^6$) octet shell (37 - 39).
As Didymium is a mixture of two rare earth elements—praseodymium and Neodymium, which were separated by A. Von Welsbach in 1885. The spectra of \( \text{Pr}^{3+} \) and \( \text{Nd}^{3+} \) in different salt have been well studied by many workers (23, 30, 33, 35-43).

The spectrum arises in the case of \( \text{Pr}^{3+} \) ions from the rearrangement of two electrons in \( 4f^2 \) configuration. The lines are emitted as a result of transitions from different excited state \( 3_{Po}, 1, 2, 3 \ldots \ldots \ldots \ldots 1_{D_2} \) etc. to the ground state \( 3_{H_4} \) as given by Hund's rule (39, 44).

The \( \text{Nd}^{3+} \) ions contain three electrons which give rise to the spectrum belonging to the \( 4f^3 \) configuration. The ground state is \( 4_{Ig/2} \) and different excited states allowed by R-S coupling fall into two group consisting of doublets and quartettes as given by – 2 \( (P, D, F, G, H, I, K, L) \) and 4 \( (S, D, F, G, I) \) respectively (45).

As Didymium is a mixture of two rare earth elements, the line emission may be characteristic of one or both. In nature, the abundance of Nd in Di is roughly four times as large as that of Pr (38). The salts of Pr are green or bluish green and those of Nd red. The Dinitrate used in the present studies was predominantly reddish with a violet touch. Hence the line spectrum may be predominantly due to Nd. Pringsheim (35, 46) studied the fluorescence of Nd, & Pr glasses and found that fluorescence of Nd glasses was weak but many Didymium glasses show strong fluorescence of the Nd type. Further, if the lines were emitted by a mixture of elements in the ratio 1:4, the intensity of some of the
lines due to one should becomes maximum at different concentration of Didymium. But in the present case as the concentration of Didymium is increased the intensity of the line emission increases as a whole and becomes maximum at about 0.01 gm of Di and intensity of all the lines starts decreasing at higher concentrations of Di. Therefore, the line spectrum is more likely due to the transitions in the luminescence centers formed by the presence of Nd in CaS lattice. However, because of the complex nature of the spectra, it is difficult to ascertain the transitions responsible for various lines.

(C) Fluorescence Spectra: Fluorescence spectra emitted as a result of one or more spontaneous transition were recorded photographically as described in Chapter V. The incorporation of Ce in CaS:Di phosphors gives the double band peaking around 5125 and 5775 Å. Both bands appear at all the concentration of Ce and only suppressed at very low and at very high concentration of Cerium. At the optimum concentration of Cerium both the bands as well lines give maximum intensity.

The inclusion of Di in CaS:Ce gives line spectra in the orange-red region. In the present case only three groups of lines have been observed. The wavelength of lines in the spectra lie in the range 5600 Å to 6500 Å. The wavelengths are given in Table No. 6.2 for ready reference with comparative intensities.

The second group of lines and third group of lines are superimposed on a continuous background. In the second group the background is due to the Cerium second yellow band peak at
<table>
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<tr>
<th>S. No.</th>
<th>Group I</th>
<th>Group II</th>
<th>Group III</th>
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</tr>
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</tr>
<tr>
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</tr>
<tr>
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</tr>
<tr>
<td>8</td>
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</table>
at 5775 Å as observed in the phosphor without Didymium (DA-0 sample).

The third group of lines observed consist of rather the narrow diffuse bands not clearly resolved and wavelengths merely denote the place where they appear darkest to the eye on the photographic plate. Most probably the lines of third groups are superimposed on the band which is given by host lattice. This red band is observed by many workers in this laboratory and attributed to some other lattice defect in the CaS: (47-49).

(D) Phosphorescence Spectra: The phosphorescence spectra, which is due to the reemission of previously observed light and persists for some time after the cessation of exciting light, are similar to the fluorescence spectra in the present investigation. In this case only weak lines are not observed at both the sides of the optimum concentration of Di and Cerium.

The variation of intensity of fluorescence lines and bands in CaS:Di;Ce phosphors with increase in activators concentration as determined by microphotometer, are given in Chapter V in Table No. 5.1 to 5.4.

As regards the variation of wavelengths with activator concentrations in both the series, no appreciable change is observed. Similar observation have been made by Dave (49) in the case of CaS:Sm, Di phosphors and by Malhotra (17) in the case of CaS:Di, Zr.

The increase in the concentration of Ce does not shift the peak towards longer wavelengths appreciably. The
increase in the concentration of Di also does not lead to the shift of the peak of this band. As the concentration of Di increases the intensity of lines increases up to an optimum concentration but the height of the band does not change appreciably. But for very high concentration of Di the yellow band is quenched along with the orange-red emission. Therefore, it is apparent that no sensitization of luminescence takes place and Ce and Di probably give rise to rather independent luminescence centers in CaS lattice.

In the present investigation, in general, the lines and band grow in intensity with increase in the concentration of activators and reach maximum at their optimum concentrations. Thereafter they decrease with increase in the concentration and the quenching region starts. This type of concentration quenching is well known in luminescence and has been explained as due to "overlapping field" of pairs of activator atoms in close proximity(50). It has been proposed by Johnson & Williams (51) that this could be explained if it was assumed that non-radiative recombination would result whenever two activator ions are present at nearest neighbour sites. But the suggestions of Dextur & Schulman (52) appear more plausible, that the direct resonance transfer of energy takes place from one activator ion to another and the dissipation takes place at certain sites in the crystals.

6.5 CONCLUSIONS:

From the above discussion we arrive at the following conclusions:

(i) The phosphors CaS:Di, Ce follow the hyperbolic decay law which may be represented by \( I = I_0 t^{-b} \), where \( b \) depends little upon the activator concentrations.
Correlation between decay and thermoluminescence justifies the validity of the eqn: \( p = S \exp \left( - \frac{E}{kT} \right) \).

The resultant decay occurs as a result of superposition of various exponentials, the kinetics being monomolecular in character.

Randall & Wilkins theory is applicable in the present case. A close agreement between the trap depth values obtained from the thermoluminescence and decay studies shows that one group of traps distribution is present and justifies the applicability of the theory.

The trap depth calculated from the two studies do not depend on the activator concentration. The study at room temperature does not reveal formation of any new trap group. It is probable that the traps observed are associated with defect other than those due to the activator ions.

Both fluorescence and phosphorescence spectra consist of bands emitted by Ce and lines due to Di. The lines observed are probably due to Nd atoms.

Both the series studied show the phenomenon of concentration quenching and there is no sensitization.

The above studies do not lead to a complete understanding of the CaS:Di, Ce system. The thermoluminescence and decay studies at other temperatures than the room temperature are necessary to obtain information about shallow & deep lying traps. Further the study of emission and absorption spectra at low temperature and paramagnetic resonance may give the information about the type of crystal field experienced by the rare earth ion, the levels involved in the luminescence transitions and the valency state of the activator ions respectively.
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