8.1 Introduction :

This chapter is devoted to the general discussion of the results obtained in the present investigation. Although some results drawn from specific studies have been described at the end of preceding chapters. They are now summarized and further discussed in the light of existing theories.

The purpose of the present work was to study the luminescent behaviour of Dy and Tb activated Calcium sulphide phosphors. The experiments done involved absorption, emission, decay, thermoluminescence and temperature dependence.

8.2 Absorption :

Absorption of Dy$_2$O$_3$ (pure activator) is at 275, 300, 350, 350, 400 and 430 m$\mu$. This may be due to characteristic absorption between 4f-5d orbits of the ion. In the case of CaS (pure), absorption is in the region 270 to 450 m$\mu$. Absorption edge in this case has been found to be at 298 m$\mu$ (4.15 eV). When flux is included in pure CaS a new absorption hump arises at 325 m$\mu$ and absorption edge has been found to be at 3.97 eV. Thus fundamental absorption of CaS shifts towards longer wavelength possibly due to local lattice deformations. Shifting of absorption edge has been supported by the work of Lehmann$^1$ in CaS host lattice. Inoue$^2$ has observed the shift in absorption band towards longer wavelength on addition of Li to MgO as a flux. This he ascribes to the formation of a defect.
structure (Li\(^+\)). Although we have no other evidence of such a type of defect in CaS lattice, we can argue that local lattice deformations in the lattice due to addition of flux may be responsible for a shift in the absorption band.

We found that the fundamental absorption of Calcium sulphide shifted from 4.15 to 3.81 eV (Fig. 3.4) at high concentrations of Dysprosium. Similarly the shift from 4.15 to 3.73 eV at high concentrations of Dy and Tb may also be due to local lattice deformations. Such a shift has also been observed by Rebane et al.\(^3\) at energies above 3.0 eV when Cu\(_2\)S (0.1 mole\%) and CuCl (0.1 mole\%) are added to CaS (activation in sulphur atmosphere at 1100\(^\circ\)C) which they ascribe to an association of calcium and sulphur vacancies. As in ZnS phosphors where often an association of donors (electron traps) and acceptors (luminescence centres) appears, much evidence can also be found in CaS pointing to a donor-acceptor interaction. This evidence appears in the shifts in the stimulation bands when different activators are used.

It has been observed that CaS obtained from different sources shows a variation in reflection characteristics. This is also true with MgO, MgS, SrS and BaS etc. Although the bulk band gap of MgO is 8.7 eV,\(^4\) Zecchina et al.\(^5,6\) reported the absorption edge of MgO at 4.58 eV. Coluccia et al.\(^7\) interpreted
that such a reduced value of absorption edge is due to the presence of local surface states intrinsic to oxides which correspond to ions in sites of unusually low coordination or the presence of high index planes on the surface. They also calculated the values for surface band gaps on the surface \langle 100 \rangle plane and on higher index planes corresponding to \( Z = 1 \) and \( Z = 2 \) (the valence of the ions) for alkaline earth oxides (calculated from Madelung potential). They found it to be 8.25 eV for \langle 100 \rangle, 4.18 eV for \langle 211 \rangle surface planes corresponding to \( Z = 1 \) and 8.0 eV for \langle 100 \rangle, 1.74 eV for \langle 211 \rangle surface planes corresponding to \( Z = 2 \), in the case of MgO. The coordination number of MgO corresponding to these planes being 5 and 3 respectively.

Since CaS is ionic, band gap for higher index planes is amenable to variation. The lowering of the absorption edge and absorption over a wide range of wavelengths may therefore be on account of the presence of a large number of surface states and the presence of ions in positions of low coordination. This would also account for the wide variation in the absorption characteristics observed for CaS from different sources. It was found that CaS was a fine powder in the present case and a substantial increase in the number of surface states with decrease in particle size cannot be denied, so the behaviour exhibited with respect to range of absorption in the present case could be on account of the above mentioned facts.
Lehmann has observed absorption edge of MgS, CaS, SrS and BaS at 5.4, 4.8, 4.4 and 3.8 eV respectively which are less than the reported values. He ascribes it due to various native defects.  

8.3 Emission Spectra:

Useful information regarding the electronic transitions in the luminescence centre and the mechanism involved in the process can be gathered from the spectral distribution of a phosphor. In general emission spectra of phosphors consist of broad bands characteristic of the particular impurity present or host lattice defects. These bands are usually structureless, bell shaped and approximate to the shape of a Gaussian curve when the energy is plotted as a function of frequency. However, in the case of activators with inner incomplete shells the emission consists of lines.

In the case of rare earths the inner 4f shell, which may hold a total of 14 electrons, is well-shielded from the perturbing influence of the crystal field by the outer electron shells. As a result the energy states of the partly filled 4f shell are only slightly affected by the surrounding environment and electronic transitions between them can be observed as narrow line like bands in both emission and absorption.  

The 4f-5d transitions of trivalent rare-earths occur at
energies above most of the 4f-4f transitions. The 5d orbitals are quite well shielded by the 4f electrons, so that as nuclear charges are added through the rare earth series, the binding energy of the 5d electrons changes very little. Therefore, the 4f-5d transition energies, through the series reflect the 4f binding energies almost exclusively. The transitions are from the lowest of the 4f states and therefore, as the number of electrons increases, the configuration splitting increases. This trend continues up to the half filled shell (Gd $^{3+}$, 4f$^7$) but the eighth electron cannot be exchange stabilized and so the transition energy decreases abruptly at Tb $^{3+}$ (4f$^8$). Then the same trend is repeated in the 2nd half of the series. The spectra due to these transitions occur at energies from 4 to 8 eV.\textsuperscript{11}

States with completely or half filled electron shell are very stable. For example, the excited states of Gd $^{3+}$ (4f$^7$, hence half filled) lie at a higher energy level. In the case of Tb $^{3+}$ (4f$^8$, half filled plus one) 4f shell readily releases an electron and the transition $4f^8$ $\rightarrow$ $4f^7$ 5d takes place at relatively low energy, while in the case of Eu $^{3+}$ (4f$^6$, half filled less one) the 4f shell readily accepts an electron and thus the charge transfer state has a low energy. Similarly in the case of Dy $^{3+}$ (4f$^9$, half filled plus two) the transition takes place at a relatively low energy.
8.3(a) Optical transitions between 4f levels:

The emissions of the trivalent rare-earths originate in transitions between the energy states of the partly filled and well shielded 4f shell. Such transitions are in principle strictly forbidden. This is because the parity of the wavefunction of the electrons does not change (Laporte's selection rule). Because the \( 7F \) and \( 5D \) states both originate from the \( 4f^5 \) configuration, they have the same parity. This implies that only weak magnetic dipole transitions (\( J = 0, \pm 1 \) with \( J = 0 \rightleftharpoons 0 \) forbidden) are allowed.

Because of spin orbit coupling it is necessary to consider the \( 7F \) states as being composed of pure \( 7F \) states with a slight "admixture" of the pure \( 5D \) state. Consequently this spin prohibition no longer applies so strictly. The parity prohibition can be lifted by mixing the \( 4f^5 \) configuration with a state possessing a different parity. The odd crystal field terms form the interaction responsible for this, i.e., those terms that change sign on inversion with respect to the rare-earth ion. If the rare-earth ion is located at a site of inversion symmetry in the relevant crystal lattice, then the odd crystal field terms are absent and the parity prohibition cannot be lifted.
8.3(b) Emission of CaS : Dy<sub>x</sub> Series :

It shows two distinct peaks at 490 and 580 nm which may be assigned to transitions from 4F<sub>9/2</sub> to 6H<sub>15/2</sub>, 6H<sub>13/2</sub> respectively (Fig. 8.1). The spectrum resembles that obtained by Lehmann. 1

8.3(c) Emission of CaS : Tb<sub>x</sub> Series :

In the case of CaS : Tb<sup>3+</sup>, Tb<sup>3+</sup> gives six distinct peaks at 420, 435, 450, 490, 545 and 580 nm. The first three lines are assigned to transitions from 5D<sub>3</sub> to 7F<sub>5</sub>, 7F<sub>4</sub> and 7F<sub>3</sub> of Tb<sup>3+</sup> respectively, the remaining three lines correspond to transitions from 5D<sub>4</sub> to 7F<sub>6</sub>, 7F<sub>5</sub> and 7F<sub>4</sub> respectively (Fig. 8.1).

8.3(d) Emission of Mixed Series :

Table 8.1 shows the emission intensity in arbitrary units with varying concentration of activators corresponding to their emitted peak wavelength. In the present work it has been found that when Dy is present in low concentrations (10<sup>-4</sup> to 10<sup>-2</sup> mole %) it enhances the emission of Tb and when it is present in high (0.03 to 0.05 mole %) concentration quenching effects begin to appear. Secondly when Tb is present in small (10<sup>-4</sup> to 10<sup>-2</sup> mole %) concentrations, its emission is enhanced by the presence of Dy but at higher concentrations (0.1 to 0.3 mole %).
<table>
<thead>
<tr>
<th>S. No.</th>
<th>Concentration of activator in CaS in mole %</th>
<th>Intensity in Arbitrary Units</th>
<th>Remarks</th>
</tr>
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<tr>
<td></td>
<td></td>
<td>420 nm</td>
<td>435 nm</td>
</tr>
<tr>
<td>1</td>
<td>0.01 Dy</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>2</td>
<td>0.01 Tb</td>
<td>9</td>
<td>14</td>
</tr>
<tr>
<td>3</td>
<td>Dy $10^{-2}$; Tb $10^{-4}$</td>
<td>23</td>
<td>27</td>
</tr>
<tr>
<td>4</td>
<td>Dy $10^{-2}$; Tb $10^{-3}$</td>
<td>15</td>
<td>28</td>
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<td>5</td>
<td>Dy $10^{-2}$; Tb $10^{-2}$</td>
<td>35</td>
<td>90</td>
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<td>30</td>
</tr>
<tr>
<td>9</td>
<td>Tb $10^{-2}$; Dy $10^{-2}$</td>
<td>35</td>
<td>90</td>
</tr>
<tr>
<td>10</td>
<td>Tb $10^{-2}$; Dy 0.03</td>
<td>15</td>
<td>35</td>
</tr>
<tr>
<td>11</td>
<td>Tb $10^{-2}$; Dy 0.05</td>
<td>10</td>
<td>15</td>
</tr>
</tbody>
</table>
FIG81. ENERGY LEVEL DIAGRAM OF Dy³⁺ AND Tb³⁺

(ARROWS INDICATE KNOWN EXCITATION TRANSFER INTERACTIONS RESULTING IN SENSITISED EMISSION)
of Tb, emission appears to suppress completely the Dy emission. When Tb emission is enhanced by Dy the suppression of the latter emission is natural. Hence for both low and high Tb, Dy should be suppressed. The enhancement or suppression of any peak of an activator in conjunction with another activator may be due to energy transfer. Energy may readily be transferred from the $^{4}F_{9/2}$ manifold of Dy to the $^{5}D_{4}$ manifold of Tb in CaS activated with Dy (10$^{-4}$ to 10$^{-2}$ mole%) and Tb (10$^{-2}$ mole%). The net flow of excitation is from Dy to Tb for low Dy concentrations and from Tb to Dy for high Dy concentrations. The reversal in direction is due to a rise in Dy self quenching as concentration increases. There is an overlapping of the emissions of Dy (490, 580 nm) and Tb (490, 580 nm). At higher concentrations of either of the activators, these lines are quenched. Since there is an overlap, the enhancement or quenching can be inferred only by studying the 545 nm line of Tb. Therefore the intensities of the 545 nm line are plotted as a function of concentration of Dy which indicates a maximum at 0.01 mole% of Dysprosium. The Dy emission overlaps strongly with two of the Tb lines. In order to judge the enhancement or quenching in the case of Dy we have to consider the individual contributions of Dy and Tb towards intensity in the overlapping region. This could, in principle, be done as follows.

Phosphors activated with varying concentrations of the
individual activators, Dy and Tb, could be studied with respect to the ratio of intensities of the two bands where there is overlap. If it should turn out that the ratio of 580 nm to 490 nm intensity is a constant, as is the case in many systems,\textsuperscript{14} the problem would reduce to one of solving a set of simultaneous equations. Let this ratio for Tb and Dy be $A$ and $B$ respectively. Then if the two intensities are $x_1$ and $x_2$ for Tb and $y_1$ and $y_2$ for Dy, the observed intensities can be written:

$$I_{490} = x_1 + y_1; \quad I_{580} = x_2 + y_2 = Ax_1 + By_1$$

since $A$ and $B$ are known the individual contributions to $I_{490}$ and $I_{580}$ can be computed.

However, an examination of the intensities of the 490 nm and 580 nm lines in singly activated phosphors shows that the ratio does not remain constant. In the doubly activated phosphors also, the effect of the second activator on the different emissions of the primary activator was found to be different. In the case of trivalent rare-earths the emission is generally fairly insensitive to environment and hence the ratio of intensities of two lines remains constant. However, it has been found that some transitions are "hypersensitive" to the environment of the ion.\textsuperscript{15} Such transitions have been called hypersensitive transitions. A well known example is the
$^{5}D_{0} \rightarrow ^{7}F_{2}$ transition of Eu $^{3+}$ corresponding to its red emission lines. For Dy $^{3+}$ a hypersensitive absorption transition has been observed at 7700 cm$^{-1}$ which is ascribed to a $^{6}H_{15/2} \rightarrow ^{6}F_{11/2}$ transition. It has been noted that all hypersensitive transitions rigorously obey the selection rule $\Delta J = 2$. Various theories have been presented to account for this selection rule for hypersensitivity.

The transition corresponding to the yellow emission of Dy $^{3+}$ is $^{4}F_{9/2} \rightarrow ^{5}H_{13/2}$ and thus obeys this selection rule, whereas the blue emission transition ($^{4}F_{9/2} \rightarrow ^{6}H_{15/2}$) does not ($\Delta J = 3$). The yellow Dy $^{3+}$ emission is therefore more sensitive to the surroundings than the blue Dy $^{3+}$ emission.

Therefore, while it is possible to infer enhancement or quenching of Tb emission unambiguously, it is not always possible to do so in the case of Dy.

As previously described (Chapter IV) there are three methods by which the process of energy transfer is established: (i) Life time measurement technique, (ii) Selective excitation technique, and (iii) Fluorescence enhancement technique. Out of these three methods, two methods enumerated above are out of the scope of this work due to inadequate instrumentation.

However, the third method of fluorescence enhancement is possible by which most of the energy transfer processes are
established in this laboratory. In the present work fluorescence enhancement of 545 nm line of Tb has been observed due to the presence of Dy.

Fig. 4.5 shows the mechanism of energy transfer between Dy—→Tb when both the activators are present in the lattice in equal quantities (0.01 mole%). When we observe the spectra individually, peak intensities of Dy (490, 580 nm) are 60 and 105 arbitrary units and peak intensities of Tb (490, 545 and 580 nm) are 27, 45 and 50 arbitrary units respectively. When both the activators are added simultaneously in the lattice, the intensities of 490, 545 and 580 nm peaks are 60, 200 and 150 arbitrary units respectively. The total intensities of 490, 545 and 580 nm peaks should have been 87, 45 and 155 arbitrary units respectively due to simple addition of intensities. But now the peak intensity of 490 nm has been reduced to 50 arbitrary units and peak intensity of 545 nm line enhanced to 200 arbitrary units. If the intensity enhancement is due to a simple addition then the observed intensities of the 545 nm and 490 nm peaks are unexplainable. The process is understandable only if we assume that the enhancement of the 545 nm peak may be due to energy transfer and it is possible due to the transfer of energy from $^4F_{9/2}$ manifold of Dy to $^5D_4$ manifold of Tb.

Similar type of evidence for energy transfer from Dy $^{3+}$ to Tb $^{3+}$ ions is observed by Taylor $^{15}$ in CaF$_2$, by Cabezas et al. $^{17}$
in glasses and by van Uitert et al. in tungstates with
the help of lifetime measurement technique. Holloway et al. have also observed energy transfer between Dy and Tb in sodium rare-earth tungstates by selective excitation technique.

The mechanism which governs the energy transfer process between trivalent rare-earth ions has been studied by several workers. In many cases the energy transfer is interpreted in terms of a resonance transfer mechanism due to the electrostatic multipole interaction, although in some cases nonresonant exchange mechanism is active. In the present work we have tried to clarify the mechanism involved.

As Dexter has stated, and also as the results of the calculations made by Inokuti and Hirayama indicate, it is very difficult to distinguish the dipole-quadrupole and quadrupole-quadrupole interactions from the exchange interaction by an analysis of the dependence of the intensity and decay time of donor emission on acceptor concentration. However, there are two ways to do this. The first is to take the theoretically derived correlation of the energy transfer probability with the absorption oscillator strength of the acceptor into consideration. As suggested by Dexter, the transfer probability is proportional to the overlap integral of the donor emission spectrum and acceptor absorption spectrum.
There is, however, a difference with respect to the definition of the overlap integral between the cases of the multipole and exchange interactions which limits its use. A second way to distinguish between the multipole and exchange interactions is to estimate "critical transfer distance" ($r_c$) and to examine whether they have appropriate values. Usually multipolar processes are responsible for remote interactions, while exchange may be important for interactions involving near neighbours.

The normalised emission per emitter ion as a function of concentration of Dy and Tb indicates that non-radiative losses are proportional to $r_c^{-6}$ (where $r_c$ is the distance between emitter and quencher) in each case and hence are attributable to d-d interaction. An estimate of critical distance of energy transfer has also been made by the following formula.

$$r_c = 2 \left( \frac{3V/4\pi X_c N}{N} \right)^{1/3}$$

(8.1)

where $X_c$ is the critical concentration and $N$ the number of ions in the unit cell. In the case of Dy and Tb, optimum concentration comes out to be (0.05 mole%) and (0.1 mole%). Substituting these values of concentration in the above expression, critical transfer distance comes out to be 55 Å and 44 Å for Dy and Tb respectively.

On the basis of these arguments, we may rule out the possibility that the exchange interaction is operative, or we can at least conclude that even if there is some contribution
of the exchange interaction, it is very small. From Table 8.1 an interesting result is observed which is discussed below. If a graph is drawn between intensity in arbitrary units Vs. concentration of Tb in ascending order, for 435 and 545 nm lines of Tb we observe a precipitous quenching of 435 nm line and a profound enhancement of 545 nm line at 0.01 mole % of Tb. The possible explanation for this mechanism may be because of the resonant (cross-relaxation) interaction between the transitions \( ^5D_3 \rightarrow ^5D_4 \) and \( ^7F_5 \rightarrow ^7F_0 \) in Tb \( ^{3+} \) ions. The 435 nm line belongs to \( ^5D_3 \) excited state of Tb \( ^{3+} \) and 545 nm line belongs to \( ^5D_4 \) excited state of Tb \( ^{3+} \). The probability of the emission from the \( ^5D_4 \) excited state increases with increasing concentration of Tb. Such a phenomenon has been observed by Gurvich et al.\(^{23}\) in inorganic phosphors activated with rare-earths. In this laboratory Tripathi et al.\(^{24}\) have also observed a profound quenching in \( ^5D_3 \) state of Tb, which they ascribe it to \( d-q \) interaction.

8.3(e) Concentration quenching :

The mechanism by which energy is transferred from one kind of centre to another kind by a process of resonance or radiationless transfer is called sensitized luminescence. The resonance may be either exchange regulated or controlled by an electric multipole process.
When the concentration of activator in a singly activated phosphor is increased beyond a certain value, it is generally observed that luminescence intensity decreases. This phenomenon known as concentration quenching has been observed in the present systems i.e., CaS : Dy and CaS : Tb. Quenching is observed above 0.05 and 0.1% for Dy and Tb respectively. The phenomenon is considered to be equivalent to thermal quenching and nearness of another activator lowers the activation energy for a non-radiative transition to the ground state. It is believed that energy is transferred from activator to activator till reaches an energy sink where the system relaxes to the ground state by phonon emission.

8.3(f) Site of activator and charge compensation :

The Tb and Dy ions occur in phosphors as Tb$^{3+}$ and Dy$^{3+}$, which is the usual valence state for most rare-earths.

The activator ion can occupy either substitutional (S) site or interstitial (I) site in the host lattice. To occupy a substitutional site the difference between the ionic radii of the activator ion and that of the host lattice cation should be within 15%. The ionic radii of Ca$^{2+}$, Dy$^{3+}$ and Tb$^{3+}$ are 0.99, 0.91 and 0.92 Å respectively. As the ionic radii of Dy$^{3+}$ and Tb$^{3+}$ ions differ by only 8.1% and 7.1% from the radius of Ca$^{2+}$ ion it is more probable that both the activators will occupy substitutional sites in CaS.
Trivalent ions can replace Ca$^{2+}$ and since rare-earths are generally trivalent some mechanism must be found to maintain the charge neutrality of the crystal. There can be three possibilities. One of them may be that two Ca ions are replaced by one $3^+$ ion and one $1^+$ ion, preserving neutrality. A second possibility can be the replacement of three Ca ions by two $3^+$ ions and the third possibility is the replacement of one Ca$^{2+}$ ion by one $3^+$ ion and excess $1^+$ charge can be compensated by $1^-$ ion at a nearby interstitial site. In the preparation of CaS : Dy and CaS : Dy : Tb phosphors, it was experienced that addition of sodium oxysalts as flux produced poorly luminescent phosphors whereas addition of NH$_4$Cl as flux produced brighter phosphors. So the first possibility which requires alkali metal ion for charge compensation is ruled out because addition of sodium oxysalts as flux could not produce bright phosphors. In this laboratory some workers$^{25,25}$ have used CaCl$_2$ as flux in CaO and CaS activated with rare-earths and prepared efficient phosphors. In all of the above mentioned phosphors halide seems to be common in the phosphor preparation. Hence it turns out that the halide acts as an efficient flux. Second possibility which requires no charge compensation is also ruled out because for efficient phosphor preparation halide flux is indispensable.$^{27}$ Therefore,
the chance for the third possibility to operate is fair because halide is necessary for efficient phosphor preparation. The halide ion may enter into the lattice interstitially preserving the charge neutrality of the crystal in the present case.  

8.4 Nature of decay and Trap distribution:

The decay curves corresponding to first order kinetics is exponential in shape and the intensity at any time can be given by:

\[ I = I_0 \exp(-pt) = I_0 \exp(-t/\tau) \]  

(8.2)

where \( \tau \) is the life time of excited state of the centre. Such type of decay is little affected by a change in the temperature of the phosphor or conditions of excitation.

Phosphors having long duration phosphorescence usually exhibit a power law decay. The decay rate not only depends upon the intensity of excitation but also on the temperature of the phosphor. The second order decay is represented by the equation:

\[ I = I_0 t^{-2} \]  

(8.3)

None of the phosphors in the present study obey Eqns. (8.2) or (8.3). Hence these equations cannot be utilized to
infer the specific process involved. Further the decay curves on the log-log plot give straight lines and the slope is not equal to two. Thus the present form of decay can be represented by the equation:

\[ I = I_0 t^{-b} \]  

(8.4)

where \( I_0 \) and \( I \) are the intensities at the start of decay and at time \( t \) respectively and \( b \) is the decay constant whose value was found to lie between 0.25 and 0.81. The deviation of this constant from unity indicates that the trap distribution is not uniform. The value of linear correlation coefficient 'r' between log I and log t has also been calculated which comes out to be nearly unity. The sign of 'r' is negative indicating that log I decreases as log t increases.

The after-glow emission of some of the phosphors such as Calcium halophosphate containing Mn and Sb, Calcium silicate activated by Mn and Pb, and ZnS103 activated by Mn have been observed in multistages by Studer et al.\(^{29}\) and Gergeley\(^{30}\) respectively. In all these phosphors the first stage decays very rapidly and then is followed by another slow decay component, all stages being exponential in nature. The different decay components may be considered as due to the traps of different depths. Thus it is reasonable to assume that as the number of exponentials increases the decay curve changes from a straight
line to a hyperbolic curve on a semi log plot. The minimum number of exponentials required to form a hyperbolic curve is three. Bube's analysis of the decay curve appears to be in agreement with this idea. Thus the 'hyperbolic decay' of phosphors containing traps of different energies and populations can be explained on the basis of Randall and Wilkins' monomolecular theory. According to this theory such a hyperbolic decay is the resultant of a superposition of exponentials corresponding to different groups of traps and can be expressed by the equation:

\[ I = I_{01} \exp(-p_1t) + I_{02} \exp(-p_2t) + I_{03} \exp(-p_3t) + \ldots \]

\[ I_{0n} \exp(-p_n t) \] (8.5)

where \( I_{0n} \) is the phosphorescence intensity due to electrons in traps of energy \( E_n \) and

\[ P_n = S \exp \left(-\frac{E_n}{kT}\right) \] \( \ldots \) (8.6)

where \( P_n \) represents the transition probability of an electron escaping from a trap of depth \( E_n \).

In fact the interpretation of phosphorescence is so complex that it is not always possible to assign a specific mechanism to the processes involved.

To obtain an idea about distribution of traps, the decay curves were analysed into a set of exponentials following Bube.31
and others. In the present case decay curves are peeled off normally into three exponentials. The trap depths were calculated from the slope of these exponentials using the following formula:

$$E = 2.303 kT \left( \log_{10} S - \log_{10} p \right)$$

$$\text{where } p = \frac{\log_{10} I_2 - \log_{10} I_1}{t_2 - t_1} \times 2.303$$

(8.7)

The values of trap depth are given in Table 5.1. The decay is assumed to be monomolecular to a first approximation in the above method of finding trap distribution. As is evident from Table 5.1, the trap depths corresponding to the three components are fairly constant in the series studied. This indicates that activators do not introduce any new trapping levels. Further the work on CaS in this laboratory using various activators and without activators had similar trapping energies. This is evident from Table 8.2. Thus it is concluded that trapping states are not associated directly with activator or coactivator and they may be attributed to host lattice defects.

8.5 **Thermoluminescence**

In spite of the advantage that this method gives direct information about the trap distribution it has certain limitations which are discussed below. It is not possible to use thermal de-excitation to study deep traps whose maximum
<table>
<thead>
<tr>
<th>S.No.</th>
<th>Host and Activator</th>
<th>Trap depth range (eV) Decay study</th>
<th>Trap depth range (eV) TL study</th>
<th>Reference</th>
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<td>1</td>
<td>CaS:Zr:Mn</td>
<td>0.55 - 0.74</td>
<td>0.77 - 0.81</td>
<td>V.K. Mathur, Ph.D. Thesis, University of Saugur (1952)</td>
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<td>2</td>
<td>CaS:Bi,Na₂SO₄</td>
<td>0.57 - 0.71</td>
<td>0.59 - 0.55</td>
<td>S. Sivaraman, Ph.D. Thesis, University of Saugur (1955)</td>
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<tr>
<td>3</td>
<td>CaS:Bi:Zr</td>
<td>0.73 - 0.77</td>
<td>0.75 - 0.75</td>
<td>S.P. Sahgal, Ph.D. Thesis, University of Saugur (1957)</td>
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<td>0.59 - 0.73</td>
<td>J.L. Thakur, Ph.D. Thesis, University of Saugur (1958)</td>
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<tr>
<td>9</td>
<td>CaS:Bi:Th</td>
<td>0.59 - 0.71</td>
<td>0.70 - 0.75</td>
<td>V.G. Macwe, Ph.D. Thesis, University of Saugur (1959)</td>
</tr>
<tr>
<td>10</td>
<td>CaS:Zr:Ce</td>
<td>0.61 - 0.55</td>
<td>0.62 - 0.55</td>
<td>C.K. Naigaonkar, Ph.D. Thesis, University of Saugur (1959)</td>
</tr>
<tr>
<td>11</td>
<td>CaS:Eu</td>
<td>0.50 - 0.54</td>
<td>0.62 - 0.55</td>
<td>R.K. Shrivastava, Ph.D. Thesis, University of Saugur (1972)</td>
</tr>
<tr>
<td>12</td>
<td>CaS:Mn:Ce</td>
<td>0.59 - 0.58</td>
<td>0.57 - 0.69</td>
<td>C.B. Telang, Ph.D. Thesis, University of Saugur (1972)</td>
</tr>
<tr>
<td>13</td>
<td>CaS Fired</td>
<td>0.62</td>
<td>0.61</td>
<td>S.N. Ekboe, Ph.D. Thesis, University of Saugur (1973)</td>
</tr>
<tr>
<td></td>
<td>CaS:CaCl₂(Flux)</td>
<td>0.70</td>
<td>0.75</td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>CaS:Er:Cu</td>
<td>0.62 - 0.70</td>
<td>0.50 - 0.71</td>
<td>C.S. Gupta, Ph.D. Thesis, University of Saugur (1975)</td>
</tr>
<tr>
<td>15</td>
<td>CaS:Tb:Eu</td>
<td>-</td>
<td>0.74 - 0.75</td>
<td>R.N. Tripathi, Ph.D. Thesis, University of Saugur (1980)</td>
</tr>
</tbody>
</table>
glow range lies in the region of the temperature of quenching. Moreover reliable determination of trap depths can only be made if they differ from each other appreciably. If a phosphor contains several closely spaced levels, only a rough estimate of trap depth is possible from the glow peak temperature. Further more the method requires a knowledge of the frequency factor which is not known precisely and can vary over a wide range.

The magnitude of retrapping is also an unknown factor. Despite all these limitations, this method remains one of the powerful tool in luminescence research. TL is affected by the heating rate and the kinetics of recombination of charge carriers between traps and centres.

The present investigation has been carried at two different warming rates i.e., 0.98 K/sec. and 0.4 K/sec. The lower warming rate was aimed at obtaining resolution of component peaks; however at the lower warming rate the glow curves show only one peak.

(a) Evaluation of trap depth – Some of the formulae used to calculate trap depths are given below.

Randall and Wilkins' formula

\[ E = 2.303 \, kT \log_{10} S \] \hspace{1cm} (8.8)
Curie's formula:

\[ E_{(aV)} = \frac{T_G - 9.7}{475} \]

for higher heating rate
(0.98 K/sec) \( \ldots (8.9) \)

\[ E_{(aV)} = \frac{T_G - 8.2}{456} \]

for lower heating rate
(0.4 K/sec) \( \ldots (8.10) \)

Grosswien's formula:

\[ E_G = \frac{1.68 k T_1 T_G}{c} \] \( \ldots (8.11) \)

Luschik's formula:

\[ E_L = \frac{0.978 k T_G^2}{\delta} \] \( \ldots (8.12) \)

R. Chen's formulae:

\[ E_T = [1.51 + 3(\mu g - 0.42)]kT_G^2 / c \]

\[ - 1.8 + 0.42 (\mu g - 0.42) \times 2kT_G \] \( \ldots (8.13) \)

\[ E_b = [0.976 + 7.3(\mu g - 0.42)]kT_G^2 / \delta \] \( \ldots (8.14) \)

\[ E_W = [2.52 + 10.2(\mu g - 0.42)]kT_G^2 / W - 2kT_G \] \( \ldots (8.15) \)

Trap depth evaluated by several methods have been tabulated in Tables 6.3 and 6.4. Most of the values of trap depth obtained from R. Chen, Grosswien are in agreement with the values of trap depth obtained from Randall and Wilkins' and Curie's methods.

(b) Glow curves - It is found that there is no apparent
change in the general shape of the glow curves with change in heating rate. At the higher heating rate the glow curves show sharp maxima and increase in peak intensity. It is also found that the peak temperature decreases slightly with the lowering of heating rate which is in accordance with the theory of Randall and Wilkins. No further resolution is revealed at the lower heating rate. The change in activator and its concentration do not produce any appreciable change in the position and number of peaks. Moreover for all the phosphors only one peak is obtained. There is only one group of traps in the present phosphor system within the temperature range studied.

In the first series, viz., CaS : Dy\(x\) the glow peak intensity increases with the increase of activator up to an optimum concentration after which it decreases. The charge carriers released from traps recombine with luminescence centres and hence TL intensity goes on increasing up to an optimum concentration beyond which lowering of intensity takes place due to concentration quenching. This phenomenon is also exhibited by \(S_3\) series of phosphors. However, in \(S_2\) series where Dy is kept constant (0.01\%) and Tb has been added in larger concentration, glow peak intensity does not decrease even up to 0.3 mole % of Tb.

It is observed in the \(S_2\) and \(S_3\) series that glow peak intensity increases to a greater extent due to the presence of
another activator. In \( S_2 \) series glow peak intensity goes on decreasing after 0.03 mole% of Dy with 0.01 mole% of Tb. But in \( S_3 \) series concentration quenching is started after 0.03 mole% of Dy due to which glow peak intensity has shown a decreasing trend. The remarkable glow peak intensity obtained in general with most of the rare earths in Ba, Sr and Ca hosts seems at least to a first approximation to be due to the matching of ionic radii. Here in our study Dy and Tb are having nearly equal ionic radii. It may also be one of the reasons for the large glow peak intensity in our study.

For both the heating rates, the calculated values of trap depth by Randall and Wilkins' method lie between 0.50 to 0.56 eV which is in agreement with the trap depth (0.51 to 0.57) obtained from the slowest exponential (Table 8.3). Since the trap depth in the present study appears to be independent of the nature and concentration of activators, as indicated earlier, it may be associated with a host lattice defect. Dy and Tb are only changing the distribution of traps to some extent.

(c) Colour of TL and its mechanism - The traps may either be associated with an impurity or with the defects produced in crystals. In the former case, the trapping process changes the effective valence of the impurity ions.

The groups of traps involved in the present study appear to
<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Trap depth by R &amp; W method</th>
<th>Trap depth by Curie's method</th>
<th>Trap depth from slowest exponential (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Lower heating rate (eV)</td>
<td>Higher heating rate (eV)</td>
<td>Lower heating rate (eV)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Higher heating rate (eV)</td>
</tr>
<tr>
<td>S1.2</td>
<td>0.60</td>
<td>0.63</td>
<td>0.72</td>
</tr>
<tr>
<td>S1.3</td>
<td>0.52</td>
<td>0.63</td>
<td>0.74</td>
</tr>
<tr>
<td>S1.4</td>
<td>0.53</td>
<td>0.63</td>
<td>0.74</td>
</tr>
<tr>
<td>S1.5</td>
<td>0.52</td>
<td>0.65</td>
<td>0.75</td>
</tr>
<tr>
<td>S1.6</td>
<td>0.51</td>
<td>0.55</td>
<td>0.73</td>
</tr>
<tr>
<td>S1.7</td>
<td>0.61</td>
<td>0.55</td>
<td>0.73</td>
</tr>
<tr>
<td>S2.1</td>
<td>0.60</td>
<td>0.53</td>
<td>0.71</td>
</tr>
<tr>
<td>S2.2</td>
<td>0.60</td>
<td>0.53</td>
<td>0.71</td>
</tr>
<tr>
<td>S2.3</td>
<td>0.64</td>
<td>0.66</td>
<td>0.77</td>
</tr>
<tr>
<td>S2.4</td>
<td>0.63</td>
<td>0.65</td>
<td>0.75</td>
</tr>
<tr>
<td>S2.5</td>
<td>0.55</td>
<td>0.65</td>
<td>0.78</td>
</tr>
<tr>
<td>S2.6</td>
<td>0.55</td>
<td>0.55</td>
<td>0.78</td>
</tr>
<tr>
<td>S3.2</td>
<td>0.62</td>
<td>0.55</td>
<td>0.74</td>
</tr>
<tr>
<td>S3.3</td>
<td>0.54</td>
<td>0.55</td>
<td>0.75</td>
</tr>
<tr>
<td>S3.4</td>
<td>0.55</td>
<td>0.56</td>
<td>0.75</td>
</tr>
<tr>
<td>S3.5</td>
<td>0.63</td>
<td>0.55</td>
<td>0.75</td>
</tr>
<tr>
<td>S3.6</td>
<td>0.54</td>
<td>0.55</td>
<td>0.77</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.76</td>
</tr>
</tbody>
</table>

Table 8.3

Comparison between Curie, Randall and Wilkins and Decay Trap depth values
be independent of activator or its concentration. It is known that in alkaline earth oxides/sulphides the TL peaks obtained between LNT and about 500 K are often attributable to the presence of traces of impurities such as Fe, Mn, Cr etc. It is not often that these impurities have been eliminated altogether from the host materials. In such cases it is sometimes possible to identify the impurity responsible for a given group of traps by its specific action on a TL peak. If the initial concentration of impurity in the host is very low, addition of that impurity as activator enhances the TL output. If on the other hand the initial concentration is high, an addition causes localized energy levels to spread into bands and a quenching results.

It is interesting to note that the TL emission was of the same colour as that of the activator emission in the singly activated series of phosphors (visual). But when TL colour of CaS : Dy was observed through a monochromator, we could observe only 490 nm peak. Similarly, TL colour of CaS : Tb was also observed; we could observe only 545 nm emission.

We have been unable to determine if the X-ray irradiation produces any damage since no glow peaks in the region studied could be attributed to such centres. However, since radiation damage is expected to take place to a certain extent, it must be
presumed that if these defects are formed they are able to transfer their energy efficiently to the impurity centres.

Further, the selective effect of the activator on the TL peak indicates either an increase in the number of trapping centres irrespective of whether it is Dy or Tb or a better transfer of recombination energy to the rare earth centres. Bhasin and Sasidharan have studied the TL of Mg$_2$SiO$_4$ : Tb and reported that the three observed glow peaks are characteristic of Tb$^{3+}$ emission, although they differ significantly in the relative intensities of various wavelengths. They have attributed the difference to the local environment in the crystal lattice which affects the transition probability of 4f electrons. In the present study we could observe only the 545 nm line of Tb. In fluorescence the 545 nm line was the most intense of the lines of Tb. After dispersion, the TL intensities of other lines are not apparently strong enough to be recordable.

Nambi et al. have studied both TL and TL spectra of a large number of rare-earth activated CaSO$_4$ phosphors. In contrast to the general nature of the glow curves, the TL spectra showed discrete peaks characteristic of the rare earths. Bhasin and Sasidharan have proposed a model in which the defects responsible for trapping charge carriers and complimentary recombination centres are not distributed
independently and randomly. During crystal formation, the directive forces tend to organise the defects into ordered configurations which act as potential TL units which are distributed randomly throughout the crystal. Each unit is characterised by an activation energy of the trap and a temperature at which it is emptied during a glow run. The glow peak emission is characteristic of the configuration of the unit except when the charge carriers escape the surrounding recombination centres in which event the emission characteristic of other luminescent centres is obtained.

The obvious inference of the present study is that the TL units corresponding to the glow peak are preferentially surrounded by Dy centres (490 nm) and terbium centres (emitting 545 nm) and there is an energy transfer between these units and the activator centres. This further suggests that the same centres are involved in TL as well as in fluorescence. Hence both the phosphors (CaS: Dy; CaS: Tb) have got the same group of traps associated with host crystal defects and only their distribution is changed by two different activators viz., Dy and Tb.

(d) Order of Kinetics – Hecht and Taylor 35 have analysed the TL of alkaline earth oxides using the theory of Randall and
Wilkins. They observe that in MgO all the glow peaks correspond to first order kinetics on the basis of a curve fitting technique. Randall and Wilkins' theory suggests that the kinetics is of the first or second order depending on whether the electron or hole which is excited remains in the vicinity of the luminescence centre, the two acting as a single unit or whether the displacement is large enough for them to recombine independently.

In the present system, it can be presumed that the site of recombination is close to the activator site on the basis of the transfer observed and discussed earlier. However, we have calculated the shape factor for some of the samples and obtained that many of the values are nearer to 0.42 indicating a first order process (Table 8.4).

For further verification we have applied the method of Muntoni et al.\(^\text{37}\) for finding the order of kinetics which is as follows:

\[
\log \frac{I(T)}{[S(T)]^\lambda} = - \frac{E}{kT} + C \quad \text{(8.16)}
\]

According to Muntoni

where \(I(T)\) is the TL intensity at temperature \(T\) and

\[C = \log \left[ \left( \frac{A s}{(1+\lambda)} \right)^{\beta^n} \right]\]

where \(\beta\) is the uniform heating rate. Value of \(\lambda\) corresponding to linear plot of

\[\log \frac{I(T)}{[S(T)]^\lambda} \text{ Vs. } 1/T\]

represents the order of kinetics.
<table>
<thead>
<tr>
<th>S.No.</th>
<th>Sample No.</th>
<th>Shape factor at lower heating rate</th>
<th>Inference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>S.1.2</td>
<td>0.34</td>
<td>First order</td>
</tr>
<tr>
<td>2</td>
<td>S.1.3</td>
<td>0.43</td>
<td>First order</td>
</tr>
<tr>
<td>3</td>
<td>S.1.5</td>
<td>0.53</td>
<td>Second order</td>
</tr>
<tr>
<td>4</td>
<td>S.1.6</td>
<td>0.49</td>
<td>First order</td>
</tr>
<tr>
<td>5</td>
<td>S.1.7</td>
<td>0.37</td>
<td>First order</td>
</tr>
<tr>
<td>6</td>
<td>S.2.3</td>
<td>0.44</td>
<td>First order</td>
</tr>
<tr>
<td>7</td>
<td>S.2.4</td>
<td>0.41</td>
<td>First order</td>
</tr>
<tr>
<td>8</td>
<td>S.2.5</td>
<td>0.48</td>
<td>First order</td>
</tr>
<tr>
<td>9</td>
<td>S.3.3</td>
<td>0.45</td>
<td>First order</td>
</tr>
<tr>
<td>10</td>
<td>S.3.5</td>
<td>0.41</td>
<td>First order</td>
</tr>
<tr>
<td>11</td>
<td>S.3.6</td>
<td>0.50</td>
<td>Second order</td>
</tr>
</tbody>
</table>
involved and the slope of the straight line thus obtained gives the value of the trap depth.

But we have used the method in a slightly different manner. We got calculated the values of $1/S$ to $1/S^2$ taking fractional powers into account; by means of a microprocessor (DCM Spectrum 7). Correlation coefficient was calculated for $\log \frac{1}{S^\alpha}$ and $\frac{1}{T}$ for different values of $\alpha$. The value of $\alpha$ corresponding to a correlation coefficient of $-1$ is taken as the order of kinetics. These values of correlation coefficient for some of the samples are tabulated in Table 8.5.

We may conclude that the order of kinetics is between 1 and 1.2. Even in the samples in which shape factor approximates to 2nd order kinetics, Muntoni's method has assigned them to a 1st order.

According to the model proposed for the TL process, a close association between a TL unit and activator is envisaged. Since the activator is trivalent, it is possible that cation vacancies may be associated with these for purposes of charge compensation. These vacancies could act as hole traps. There would of course be other vacancies produced on account of thermodynamic necessity which are not associated with the activator. The first order mechanism proposed earlier is not inconsistent with this picture. An value of 1.2 would then
### Table 8.5
Order of Kinetics by Muntoni's method

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Sample</th>
<th>Heating Rate</th>
<th>Correlation Coefficient between log $1/S$ and $1/T \times 10^{-5}$ (1-ve)</th>
<th>Inference</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>$S_{1.2}$</td>
<td>HBR</td>
<td>0.999 0.998 0.993 0.972 0.930 0.855 0.775 0.710 0.559 0.438 0.341</td>
<td>Ist order</td>
</tr>
<tr>
<td>2</td>
<td>$S_{1.5}$</td>
<td>HBR</td>
<td>0.954 0.948 0.944 0.939 0.936 0.925 0.885 0.822</td>
<td>Descending - 0.575</td>
</tr>
<tr>
<td>3</td>
<td>$S_{1.5}$</td>
<td>LHR</td>
<td>0.907 0.825 0.730 0.530 0.352 0.093</td>
<td>Descending ---</td>
</tr>
<tr>
<td>4</td>
<td>$S_{1.6}$</td>
<td>LHR</td>
<td>0.945 0.939 0.914 0.877 0.824 0.753 0.543 0.421 0.544 0.479 0.378</td>
<td>Ist order</td>
</tr>
<tr>
<td>5</td>
<td>$S_{2.2}$</td>
<td>LHR</td>
<td>0.951 0.853 0.787</td>
<td>Descending ----------------------</td>
</tr>
<tr>
<td>6</td>
<td>$S_{2.4}$</td>
<td>LHR</td>
<td>0.950 0.892 0.824 0.594</td>
<td>Descending ----------------------</td>
</tr>
<tr>
<td>7</td>
<td>$S_{2.5}$</td>
<td>HBR</td>
<td>0.954 0.975 0.982 0.970 0.959 0.939</td>
<td>Descending ----------------------</td>
</tr>
<tr>
<td>8</td>
<td>$S_{3.2}$</td>
<td>HBR</td>
<td>0.970 0.980 0.988 0.985 0.971 0.946 0.912 0.946</td>
<td>Descending -------</td>
</tr>
<tr>
<td>9</td>
<td>$S_{3.4}$</td>
<td>LHR</td>
<td>0.995 0.993 0.994 0.983 0.953 0.900 0.823 0.716 0.580 0.427 0.251</td>
<td>Ist order</td>
</tr>
<tr>
<td>10</td>
<td>$S_{3.5}$</td>
<td>HBR</td>
<td>0.973 0.966 0.902 0.897 0.960 0.927 0.893 0.859 0.810 0.725 0.659</td>
<td>1.1 order</td>
</tr>
</tbody>
</table>

LHR = Lower heating rate;  HBR = Higher heating rate.
be due to a predominantly first order process with a slight
admixture of a second order process on account of the spatial
distribution of traps and recombination centres.

8.4 Frequency factor and size of the trap

The trap depth was calculated for a few samples of
each series at the higher heating rate by initial rise method
(Garlick and Gibson) which is independent of the order of
kinetics. The value of trap depth was found to be 0.73 eV
which was substituted in the following equation.

\[
\frac{E}{kT_0^2} = S \exp\left(-\frac{E}{kT_0}\right)
\]  .. (8.17)

which gave the value of \( S \) of the order of \( 7 \times 10^9 \) sec. This
is of the same order as obtained by Randall and Wilkins for
alkaline earth sulphide phosphors and used by several other
workers (Table 8.2). The size of the trap has been
calculated as follows.

From semiconductor theory the attempt to escape frequency

\[
S = N_C \delta v
\]  .. (8.18)

where \( N_C \) is the density of states in and near the bottom of
the conduction band. \( \delta \) is the capture cross-section of an
empty trap and \( v \) is the thermal velocity of the charge carrier.
The relation between $S$ and $S$ can be given as

$$\frac{S}{S} = 1.5 \times 10^{25}$$

So knowing the value of $S$, the size of the trap can be estimated approximately and it turns out to be $4.65 \times 10^{-7} \text{ cm}^2$ in the present case which for ZnS phosphors is of the order of $10^{-16} \text{ cm}^2$. The trapping cross-sections estimated for various substances have values from $10^{-11} \text{ cm}^2$ to $10^{-24} \text{ cm}^2$ and hence in the present case the traps appear to be of medium size.

8.7 Correlation between Thermoluminescence and Decay

In general the decay of phosphorescence is recorded at room temperature up to a sufficiently low intensity but not zero. Consequently traps associated with the fastest decay and other exponentials are emptied, leaving these associated with the slowest exponential not fully emptied. In thermoluminescence even, if the glow curve recording is started before the intensity of decay is brought to zero, the glow maximum has major contribution from the traps corresponding to the slowest exponential which are not fully emptied in the decay experiment and thus the trap depth from the glow experiment should be a little higher than that calculated for the slowest exponential in decay studies. In the present case the values of trap depth
as obtained by Curie's method are a little higher than those for the slowest exponential in the decay studies as is to be expected (Table 8.3). But the values obtained by Randall and Wilkins' method are not higher owing to the omission of the $f(\beta, S)$ term (equivalent to 0.1). Moreover since we take the TL after cessation of excitation and allowing the phosphor to decay for a considerable time (5 minutes) it can be expected that only the slowest exponential in the decay curve is operative. Several experimentalists in TL have observed that the phosphorescence decay at any temperature corresponds to the trap group immediately above it in temperature. The correlation between TL and decay is also evident when the ambient temperature of observation is increased. It is observed that the decay becomes faster and TL output is also decreased. Similar observations have been made by Moharil and others.

3.8 Temperature dependence of emission:

Investigations on temperature dependence of the fluorescence intensity of phosphors are of great interest as in combination with other pertinent data, they yield qualitative and sometimes also quantitative insight into the mechanism of luminescence. Increasing the temperature of a phosphor results
in a higher probability of radiationless transitions within the activator ions. Consequently for all phosphors temperature quenching occurs. The temperature at which the quenching occurs provides information about the interaction of the activator ions with the surrounding host lattice ions. This interaction is small when the transitions occur in an inner shell as in the case of rare earth activated phosphors which consequently possess a high quenching temperature. For example the quenching temperature of Eu$^{2+}$ activated alkaline earth pyrophosphates are much lower than those found for most Eu$^{3+}$ activated phosphors. The difference is reasonable as in Eu$^{3+}$ activated phosphors, in contrast to the Eu$^{2+}$ phosphors, no excitation of 4f electrons to outer shells takes place.

Maske has pointed out that there are two important factors to be considered in the temperature dependence of emission, an increasing absorption with temperature leading to a high emission and a decrease in efficiency of the fluorescence due to competing phonon processes. Because the effects work against each other, the brightness temperature curve sometimes shows a maximum, the position of which will depend on the relative importance of the two factors.

Blasse and Bril suggested that $\Delta r$, the equilibrium distance between the ground and excited states as also the radius
and charge of the cations surrounding the luminescent centre determine the quenching temperature of fluorescence to a great extent. By making reasonable assumptions concerning the parameters involved, Blasse has shown that a necessary but not sufficient condition for efficient fluorescence is that $\Delta r^0$ should be about 0.3 Å. For small values of $\Delta r$, E is large and efficient fluorescence occurs even at higher temperature.

It is possible to obtain a rough measure of $\Delta r$ from the set of radii corresponding to the principal maxima in the radial wavefunctions for atoms and ions is given by Waber and Cromer. It is thus possible to extract the difference in radii between two electron shells and the difference can be taken as a measure of $\Delta r$. For example, in Eu$^{3+}$ activated phosphors excited in the Europium charge transfer band, ground and excited states both belong to the 4f configurations so that $\Delta r$ approaches zero.

On the other hand Dy and Tb activated phosphors, excited by the 4f - 5d transition have $\Delta r = 0.24$ Å (the difference between 4f and 5d orbital radii).

8.9 Temperature dependence of fluorescence of Dy and Tb activated phosphors:

The fluorescence of CsS : Dy$_x$, CsS : Dy$_x$: Tb$_{0.01}$, CsS : Dy$_{0.01}$: Tb$_x$ phosphors first goes on increasing under X-ray excitation to a maximum and then decreases rapidly with the rise of temperature. An increase in fluorescence with
temperature can be due to several possibilities:

(a) an increase in the absorption of the incident radiation due to a change in the absorption spectrum of the host with temperature;\textsuperscript{51}

(b) a temperature dependent transfer of energy between the activator and the host;\textsuperscript{52}

(c) a change in the spectral distribution to a region of higher sensitivity of the detector;\textsuperscript{53}

(d) an emptying of traps and a consequent radiative recombination of electrons and activator centres.

Since the excitation was by X-rays, the first possibility which applies to excitation by monochromatic radiation is ruled out. If there is a temperature dependent energy transfer to any other emission centre, a rise in fluorescence intensity with temperature could take place. In the present system, for example, the Dy emission would go down fast while a second emission band would rise rapidly so that the resultant intensity could show an upward trend. Such a phenomenon has been observed in the case of CaWO$_4$:Sm and CaMoO$_4$:Sm\textsuperscript{52} where the Sm emission rises rapidly more than offsetting the quenching of WO$_4$ or MoO$_4$ emissions.

In the present system, no host emission was recordable at any stage. Besides, a temperature dependent energy transfer from host to activator would be more relevant when the excitation is
specifically absorbed by the host as in the case of UV excitation. Further this should depend on the nature of the activator used which does not seem to be the case in the present instance. Therefore, the possibility of a temperature dependent energy transfer mechanism being responsible for the observed rise in fluorescence is also remote.

Emission spectra for the phosphor CaS : Dy at different temperatures was studied. It was found that spectral distribution remained the same. Only the overall emission intensity was reduced at higher temperature. This ruled out the third possibility. It was observed that the rise in emission intensity is obtained only under dynamic conditions (increasing temperature conditions). The emission at different temperatures had however a lower intensity values than at room temperature. This indicates some additional source of charge carriers during rise in temperature. When we excite the phosphor at room temperature there is a possibility of filling traps. These traps are emptied around TL peak temperatures. Thus, the fluorescence at a particular temperature plus contribution from traps may lead to a higher emission intensity. The rise in brightness occurs at the TL peak location whence the fourth possibility may hold good in our case.

Activation energy for non-radiative transitions has also
been calculated and tabulated in Tables 7.1 and 7.2. It follows from the tables that increase in activator concentration causes a decrease in activation energy. The observed quenching can be ascribed to a gross modification of the probability of at least one of the internal transitions in the luminescent centre as a result of proximity to another identical centre. In so far as specific processes have been discussed it is usually suggested that concentration quenching is equivalent to thermal quenching and that the nearness of another activator results in a substantial decrease in the thermal activation energy for a non-radiative transition to the ground state.

810 Conclusions:

On the basis of the studies described so far the following conclusions have been drawn.

(i) The absorption edge of CaS is observed around 4.15 eV.
(ii) The line emission of CaS : Dy$^{3+}$ consists of two peaks at 490 and 580 nm which correspond to transitions:

$$^{4}F_{9/2} \rightarrow ^{6}H_{X} \ (X = 15/2, 13/2)$$

(iii) The line emission of CaS : Tb$^{3+}$ consists of six peaks at 420, 435, 460, 490, 545 and 580 nm which correspond to transitions:

$$^{5}D_{3} \rightarrow ^{7}F_{X} \ (X = 5, 4, 3)$$
and $$^{5}D_{4} \rightarrow ^{7}F_{X} \ (X = 6, 5, 4)$$
(iv) When both the ions Dy$^{3+}$ and Tb$^{3+}$ are present in CaS simultaneously, the energy is transferred from Dy$^{3+}$ to Tb$^{3+}$ by a resonance transfer mechanism possibly by d–d interactions.

(v) The values of trap depth obtained from TL studies lie between 0.40 and 0.55 eV indicating only one group of traps and they agree well with the values of trap depth determined from decay studies 0.51 and 0.57 eV (obtained from slowest exponential).

(vi) The trap depth does not show any systematic variation with activator concentration suggesting that trapping states are not associated directly with activators; hence they may be attributed to the host lattice defects.

(vii) The kinetics involved in the TL process are of first order.

(viii) $^5D_3$ manifold of Tb shows a precipitous quenching as compared to the $^5D_4$ manifold at higher concentration of Tb.

(ix) Concentration quenching for Dy$^{3+}$ (0.05 %) occurs earlier than for Tb$^{3+}$ (0.1%).

(x) In temperature dependence activation energy for non-radiative transitions decreases with increasing concentration.

(xi) Frequency factor is of the order of $\approx 10^9$/sec.

(xii) Traps are of medium size and the same group of traps are involved in decay and thermoluminescence.

(xiii) Colour of TL was observed in CaS : Dy and CaS : Tb at 490 and 545 nm respectively which also correspond to the fluorescence of the respective activators.
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