CHAPTER VII

DISCUSSION AND CONCLUSION
7.1 GENERAL:

The present investigation was undertaken on Strontium Sulphide on the trapping states and luminescence centres of CaS : Cu phosphors by the study of decay, glow-curves and spectral distribution. Formation of solid solution of CaS : SrS is also studied. This chapter deals with the interpretation and discussion of the results and their correlation with each other. The data regarding decay, thermoluminescence, X-ray study of formation of solid solution, and spectral studies are given in Chapters III, IV, V and VI respectively.

7.2 CHARACTERISTICS OF THE PHOSPHORS:

(i) General Characteristics:

The general appearance of the phosphors is greyish as seen in daylight having CaS as a major constituent (sample 1 to 6). They assume a lighter shade in the same colour as SrS is introduced. Sample Nos. 7 to 11 appear greenish grey.

The colour of these samples under excitation by ultraviolet lamp and as seen visually is bluish green for CaS : Cu
phosphor and green for the SrS : Cu phosphor. The glow colour of samples No. 2 to 4 is green, for samples No. 5 to 7 it is yellowish green and for samples No. 9 to 11 the colour is again green. The phosphorescence intensity for all the samples (phosphors) gradually decays to greenish yellow, then yellow and ultimately to orange colour.

The sulphides of Calcium and Strontium which are the starting materials for the preparation of the phosphors remain completely as sulphide after the firing process. Since all the phosphors are fired in controlled atmosphere (vacuum) there is no possibility of oxidation and hence there is no formation of oxide of the phosphors at all. This is also confirmed by X-ray diffraction study of the samples. X-ray evidence shows complete solid solution of SrS in CaS.

(ii) Defect Formation:

When the charge composed of CaS : SrS : Cu and the flux Na₂SO₄ is placed in the furnace and the firing is started, the atoms of the reactive sulphide and the activator copper present in the molten phase of flux during the firing period, are subjected to a high density of phonons in equilibrium. After the completion of the firing, the phosphor is removed from the furnace and is cooled down suddenly. The following possible defects are likely to be frozen in:-
(a) Vacancies of $\text{Ca}^{2+}/\text{Sr}^{2+}$ and $\text{S}^{2-}$ in equal number (Schottky defects).

(b) Interstitial $\text{Ca}^{2+}/\text{Sr}^{2+}$ and nearby $\text{Ca}^{2+}/\text{Sr}^{2+}$ vacancy and/or interstitial $\text{S}^{2-}$ and a nearby $\text{S}^{2-}$ vacancy (Frenkel defects).

(c) Interstitial or substitutional activator $\text{Cu}^+$ and flux ion $\text{Na}^+$.

When the charge consisting of the mixed sulphides of calcium and strontium along with the flux and activator is subjected to the heat treatment in the furnace; the formation of aforesaid defects along with exchange of $\text{Ca}^{2+}$ and $\text{Sr}^{2+}$ is possible.

(iii) **Influence of Flux:**

Gugel(1) put forward the hypothesis of solid solution formation of flux with the host lattice. The lattice spacing of numerous sulphides and selenide phosphors has been proved to be independent of the nature of flux used in preparing the phosphors. For instance, the spacing is the same in pure strontium sulphide and in phosphors prepared with flux such as $\text{LiF}$, $\text{Na}_2\text{SO}_4$, and $\text{SrCl}_2$.(2) In the present case similar results are obtained.
(iv) **Position of Activator:**

An added impurity can occupy interstitial and/or substitutional sites in the host lattice. An impurity enters substitutionally if:

(a) The electronegativity of the two ions is very close to each other\(^{(3)}\).

(b) The ionic radii of the two do not differ by more than 15%\(^{(4,5,6)}\).

In the case of substitutional impurities the concentration for quenching is high and the decay is exponential\(^{(7)}\). Interstitial substitution in phosphors requires a comparatively low concentration of impurity for quenching and the emission shows a hyperbolic decay.

<table>
<thead>
<tr>
<th></th>
<th>CaS</th>
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<tr>
<td>Optical absorption edge (eV)</td>
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</tr>
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<td>Cationic radius (Å(^{0}))</td>
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<td>1.13</td>
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<tr>
<td>Next neighbour distance (Å(^{0}))</td>
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<td>Interstitial radii (Å(^{0}))</td>
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</table>
The electronegativity of calcium and strontium as cited above are 1.04, 0.99 and that of copper is 1.92 and the ionic radii for calcium and strontium are 0.99 and 1.13 and for copper, it is 0.96 respectively. The ionic radius of Cu differs by about 3% from that of Ca and 16% from that of Sr, thus suggesting substitutional and interstitial entry of copper in the two lattices of calcium and strontium. However, the decay curve for CaS : Cu phosphor reveals a hyperbolic nature, suggesting the interstitial entry of copper in CaS. It has been reported by earlier workers that copper can have substitutional position in CaS(8,9).

As mentioned earlier the ionic radii of Sr and Cu differ by about 16% suggesting interstitial entry of copper. However, it appears that Cu with 0.96 Å radius cannot easily enter the interstices of 0.61 Å and 0.73 Å without distortion. Thus in the light of the above facts one can say that copper occupies a substitutional site both in the CaS and the SrS lattice.

7.3 PHOSPHORESCENCE DECAY:

In general, a phosphor begins to emit luminescence within $10^{-8}$ second after onset of excitation but very often much of the excitation energy is stored at metastable states or traps so that the photon emission is delayed for intervals ranging
from a few seconds to a few hours after cessation of excitation depending on the nature of the phosphor.

In copper activated ZnS phosphors the duration of phosphorescence is greatly affected by the addition of CdS. In a ZnS phosphor containing 2% of CdS, the afterglow is visible for more than an hour; in a mixed phosphor with 10% of CdS, the duration of phosphorescence is reduced to half a minute; with 30% to several seconds, while in phosphores containing 40% and more no afterglow is perceived without the use of a phosphorescope \(^{10,11,12,13,14}\).

In the present investigation also CaS : Cu phosphor exhibits phosphorescence for one minute and as the concentration of SrS is increased the duration of phosphorescence goes on decreasing. In the phosphores where SrS is a major component, very rapid decay of the order of five seconds is evident from the decay curves (figure 3.6).

After cessation of excitation there is decay of luminescence output with time as the stored energy is released. When there is a simple excitation without ionization and trapping, the luminescence intensity \(I\) decreases exponentially with time according to the equation

\[
I = I_0 \exp (-\alpha t) \quad .... (7.1)
\]
where, $I_o$ is the luminescence output at the time of cessation of excitation and $\tau$ is the decay constant, which depends on the composition and structure of the phosphor. In this case, the spontaneous exponential decay is very little affected by the change in the temperature of the phosphor or conditions of excitation. However, when the energy stored in the phosphors is in the form of trapped electrons at metastable states then the so-called power-law decay is observed which is given by

$$I = I_o t^{-b} \quad \text{.... (7.2)}$$

where, the exponent 'b' is strongly dependent on the phosphor temperature and on the intensity and duration of excitation.

The form of decay curves has most often been cited as evidence for a particular mechanism. Decay data for the sulphide phosphors are usually presented in the form of log-log plots$^{(15)}$ where the curves often approach straight lines over a large part of decay period.

In the present case, log $I$ versus $t$ curves are not straight lines, and decay curves on log-log plot give more or less straight lines over a large part of decay period with curvature at the end of decay. The curvature becomes less prominent as the percentage of SrS increases. However, the slopes of these lines are less than two. Thus the possibility of simple exponential decay with monomolecular kinetics as well
as power law decay with bimolecular mechanism can safely be ruled out. Since the nature of Log I versus t curves is hyperbolic and as Lenard et al.\(^{(16)}\) have reported that the basic nature of kinetics of luminescence in alkaline earth sulphide phosphors is monomolecular, the hyperbolic form observed can be interpreted as due to the summation of several processes with a range of values for \(p\), which is the probability factor for the release of trapped electrons and defined by Randall and Wilkins as

\[
p = s \exp\left(-\frac{E}{kT}\right)
\]

\(\ldots\) (7.3)

Garlick and Bube\(^{(17,18)}\) have attempted a direct verification of this equation. However, due to uncertainty of frequency factor this is difficult. Randall and Wilkins\(^{(19)}\) have assumed the value of 's' to be constant. But later theoretical investigations have established the fact that 's' depends on temperature \(T\) as well as on the trap depth\(^{(20,21,22)}\).

Many previous workers\(^{(22,23,24)}\), instead of assuming a particular value of 's' have calculated it from the shift of glow-curve maximum with different heating rates, as well as from Chen's formula\(^{(25)}\). However, the shift of glow-curve maximum with different heating rates being small, the accuracy of this method of estimation cannot be much stressed.
In the present investigation the frequency factor \( 's' \) was calculated from glow curves using Chen's formula, the values being listed in Table 4.1. In most of the cases, the value of \( 's' \) comes out to be of the order of \( 10^0 \text{ sec}^{-1} \) and this value has been adopted for the evaluation of trap depth from the decay curves.

The observed decay in the present case follows the power-law given by equation 7.2. It will be seen from the Table 3.1 of Chapter III (Decay) that the decay constant for the samples lies between \(-0.87\) to \(-0.99\).

In some phosphors multistage decay has been observed by some workers\(^{(26,27)}\). In these phosphors first stage decays rapidly followed by another component and all the stages are exponential in nature. It is assumed in this case that as the number of stages increases, the nature of decay changes from exponential to hyperbolic, which can be explained by a monomolecular mechanism using a superposition scheme\(^{(18)}\). Thus in the present case when the decay curves are peeled off into three exponentials (for four samples) into two exponentials (for five samples) and into one exponential (for two samples), the result of decay can be represented as:

\[
I = I_{o1} \exp(-p_1t) + I_{o2} \exp(-p_2t) + I_{o3} \exp(-p_3t) \ldots (7.4)
\]

corresponding to the three different trap-depths.
$E_1$, $E_2$, $E_3$, which are defined by equation (7.3). Of these the shallowest traps will empty soon, leading to rapid initial decay of phosphorescence, while the deeper ones will be responsible for the long duration phosphorescence.

From Table 3.2, it can be seen that the trap-depths decrease almost uniformly with increase of SrS concentration. This suggests that SrS introduces some new shallow trapping levels in the region studied. With SrS only and samples containing SrS as a major constituent, only one or two exponentials are enough to represent the decay curves. This indicates the presence of only shallower traps, and simultaneously the absence of deep traps. The deviation of decay constants from unity suggests that the distribution of traps is not uniform. However, from the values of decay constant (Table 3.1) the distribution may be assumed to be quasi-uniform.

7.4 THERMOLUMINESCENCE:

The glow curve method of investigating phosphors has been widely used as a means of investigating the mechanism of luminescence. It offers significant information about the kinetics involved in the process and is a powerful tool for evaluating the various parameters. This method, however, has
some limitations and it will not be out of place to mention them before discussing the results.

Trap-depths can be determined accurately only if these differ from each other appreciably. But in the case of phosphors containing a close distribution of traps, the individual trap-depths cannot be resolved. It is difficult to measure the true temperature of the phosphor as it is a poor conductor of heat.

The glow curves are markedly sensitive to the presence of impurities and thermal treatment. The role of CdS in the ZnS : Ni phosphor has been investigated by Elmanharawy (28). He studied the effect of mixed crystal formation and the temperature-dependence of fluorescence and thermoluminescence. He found that thermo-luminescence peaks shift to lower temperatures with increase in Cadmium concentration.

In the present investigation, thermoluminescence was studied at a single warming rate of 1.0°K/sec. The glow-curve patterns obtained are shown in figure 4.3. The thermoluminescence consists of a single peak indicating only one group of traps. In this investigation also, a shift to lower temperature is observed with increasing SrS concentration.
7.5 EVALUATION OF TRAPPING PARAMETERS:

Several methods have been suggested to determine the trap-depth from glow-curves. They have been summarised in section 4.2 of Chapter IV.

The activation energy corresponding to each glow-curve was found by applying Randall & Wilkins formula:

\[ E = 2.3026 \times K T_m \log_{10} S \quad \ldots \quad (7.5) \]

which assumes monomolecular first order kinetics.

Chen's formulae\(^{(25)}\) for general order kinetics which do not require any a priori assumptions as to the order of kinetics,

\[ E_T = \left[ 1.51 + 3.0 \ \text{(pg-0.42)} \right] \frac{K T_m^2}{T} - \left[ 1.58 + 4.2 \ \text{(pg-0.42)} \right] \times 2 K T_m \quad \ldots \quad (7.6) \]

\[ E_S = \left[ 0.976 + 7.3 \ \text{(pg-0.42)} \right] \frac{K T_m^2}{W} \quad \ldots \quad (7.7) \]

\[ E_W = \left[ 2.52 + 10.2 \ \text{(pg-0.42)} \right] \frac{K T_m^2}{W} - 2 K T_m^2 \quad \ldots \quad (7.8) \]

were also used. Here \( T_m \) is the maximum peak temperature, \( E_T \), \( E_S \), \( E_W \) are activation energies as calculated from
the half width towards the low temperature side, \( \delta \) the half width towards the high temperature side, and \( w \), the total half width. \( \mu g \) is the geometrical or shape factor given by \( \mu g = \delta / w \). The frequency factor 's' was also evaluated by using Chen's formula.

The values of the estimated trapping parameters are given in Tables 4.1, 4.2 and 4.3. From the Table 4.3 it can be seen that values obtained from Chen's formulae agree well with the values of the first exponential corresponding to the slowest rate obtained by "peeling off" procedure. On the other hand, the values calculated with Randall and Wilkins formula give slightly higher values as compared to those calculated from the first exponential in "peeling off" procedure. This indicates that the kinetics is neither purely monomolecular nor bimolecular and hence Chen's general order formulae give better agreement.

7.6 VARIATION OF ACTIVATION ENERGY WITH SrS CONCENTRATION AND SHAPE OF THE GLOW CURVES:

The values of the trap depths are found to be between 0.67 eV. and 0.51 eV. as evaluated by Chen's formulae, while those estimated by Randall and Wilkins' formula are between 0.70 eV. and 0.50 eV. Increase in the concentration of SrS results in a corresponding decrease in the values of trap-depth.
It is found that with increase in the SrS concentration, the thermoluminescence intensity is reduced. The traps in SrS : Cu phosphor are shallower than those of CaS : Cu phosphor which is evidenced by the long after glow of the latter phosphor.

In wide band gap materials, it has been observed that many physical properties such as band gap, impurity ionization energy and carrier mobility are related to the size of ions, bond distance, polarizability and electronegativity difference. The widths of allowed bands (carrier mobility) increase with the polarizability of the atoms and the dielectric constant also increases. The latter decreases the coulombic binding force of both carriers to their centres and leads to shallow donors and acceptors. The traps related to a broad allowed band are shallower than those related to a narrow one. This may explain the difference in trap depths observed in CaS and SrS where the cation radii are 0.99°A and 1.13°A respectively.

7.7 CORRELATION BETWEEN DECAY AND THERMOLUMINESCENCE STUDIES:

The correlation between the results of thermoluminescence and decay is good, when Chen's formulae are used for evaluating the trap depths. Both the studies show a complementary character. They seem to explain the nature and distribution
based on similar assumptions including the possibility of general order kinetics being applicable to the phosphor system.

7.8 SOLID SOLUTION AND X-RAY DIFFRACTION STUDY:

A solid solution may be defined thermodynamically as a single phase containing more than one species of atoms. It may also be defined physically as a material containing only one type of crystal structure wherein the identity of the atom in at least one of the lattice sites is not fixed.

On the basis of crystallographic considerations solid solution can be defined as one of the following types:

(1) Interstitial;

(ii) Substitutional.

These have been discussed in detail in Chapter V (solid solution and X-ray diffraction study). The following points are relevant to the discussion of results.

Interstitial solid solution is accompanied by distortion in the host lattice, depending upon the size of atoms as mentioned earlier. Substitutional solid solutions usually show solubility over wide range of concentrations. In continuous solid solution of ionic salts the lattice parameter is directly proportional to the solute present which is known
as Vegard's law. In figure 5.2 of Chapter V, the dotted straight line represents Vegard's law and the curve shows the positive departure from it as observed in alloys; Positive as well as negative deviations from Vegard's law have been observed in solid solutions.

**Substitutional solid solution requires:** (i) same crystal structure; (ii) ionic radii within 15%; (iii) same electronegativity and same valency.

Since in the present case the ionic radii of the Ca and Sr differ by about 13%, the crystal structures are identical (Rocksalt), electronegativities are almost the same, a continuous substitutional solid solution is expected. Solid solution may increase or decrease the lattice parameters of the compound in question, thus producing a shift of the diffraction lines. This is particularly noticeable at a higher Bragg's angle, where the line displacement is relatively large for a firm change in lattice spacing. This will lead to the appearance of additional lines. The extra diffraction lines which so appear must not be confused with presence of additional minor constituents. By accurate line shift determination by comparison method, X-ray identification of a number of lines of the solid solution can be inferred. If a substance is a mixture a clear overlapping of diffraction lines should result.
In a two component system the lattice dimensions and hence the spacing of the mixed crystal can have all values between those of the pure compounds. These values differ as much as by 6% in the case of PbCl$_2$ and PbBr$_2$ systems. For example, the spacing of the spectral line varies from 2.508Å for PbCl$_2$ to 2.635Å for PbBr$_2$ (30). Lembra (31) has also reported a maximum deviation in NaCl : KCl and KCl : KI systems. Schleede and Gantzckov have established that the alkaline earth sulphide phosphors are essentially of normal crystal structure as far as can be demonstrated by X-ray photographs (32,33). They obtained normal diffraction patterns having sharp and continuous lines. In the present case also sharp powder photographs (figure 5.3) are obtained for each sample indicating normal crystal structure. A careful observation of the photographs reveals that there is an appreciable shift in the diffraction lines for all the samples, which may be attributed to the solid solution formation.

The lattice constant for each sample has been calculated and these are listed in Table I of Chapter V. A plot between lattice constants and the mole percentage of SrS has also been given in figure 5.2. This indicates that all the samples lie on the curve showing a positive deviation from Vegard's law. This fact confirms that the solid solution of the sulphides of calcium and strontium exists over the entire range. One can conclude that the solution of SrS in CaS as
well as of CaS in SrS is of substitutional type showing change in lattice constant of the mixed sulphides.

7.9 EMISSION SPECTRA:

When an activator or any impurity ion is introduced in any host lattice either interstitially or substitutionally, it is subjected by its environment of cations to an electrostatic field. The field perturbs the ground and the excited states of the foreign atom in such a way that its energy levels are brought closer together. As a consequence, the transitions on which luminescence depends, are reduced in magnitude. The field strength is found to depend on the size of the crystal lattice and polarizability of the elements composing the crystal\(^{(34)}\). Consequently the spectral position of the emission bands should shift to longer wavelength as spacing is decreased. If the spacing is increased the shift is expected to be to the short wavelength side. The relationship was first explicitly demonstrated by Klasens \textit{et al.} for phosphors of perovskite structures and was subsequently verified by Fonda and others\(^{(34,35,36,37)}\). On the other hand, halides and sulphides of the alkali metals behave sometimes quite differently. Here an increase in cation or anion size is accompanied by a shift to shorter wavelength\(^{(38,39,40,41)}\). Fonda\(^{(34)}\) has argued that this is
chiefly due to an increase in polarizability on which the field strength of the activator environment depends.

Smith\(^{42}\) has investigated manganese activated zinc-cadmium phosphates and found that on increase of cadmium content, the band is shifted first to lower wavelengths and then to longer wavelength as compared to zinc or cadmium phosphate alone. These results have been explained as due to change in structure\(^{34}\).

The results of the emission spectra for both fluorescence and phosphorescence are given in chapter VI (Emission). It is found that in the case of fluorescence, CaS : Cu gives an emission band peaked at 4950\(^0\)A whereas in the case of phosphorescence, it gives an emission band peaked at 5575\(^0\)A. In a similar manner, SrS : Cu gives an emission band of fluorescence at 5250\(^0\)A, and in the case of phosphorescence, it gives an emission band peaked at 5615\(^0\)A. Lehmann\(^{43}\) reports emission for CaS : Cu (0.1\%) : Na(0.2\%) at 4950\(^0\)A and for SrS : Cu(0.1\%) : Na(0.2\%) at 5300\(^0\)A. Both in fluorescence and phosphorescence, the emission band begins to shift to longer wavelengths as soon as strontium sulphide is mixed in different ratios with calcium sulphide. The emission band continues to shift towards longer wavelengths until calcium sulphide and strontium sulphide are mixed in so that the molar percentage of SrS is 51.8 in CaS.
With further increase of the ratio of strontium sulphide to calcium sulphide, the emission band starts reverting back to shorter wavelengths step by step and finally it returns to the peak position corresponding to SrS : Cu.

The relative peak intensity in both the cases of fluorescence and phosphorescence, is maximum for CaS and it decreases gradually with the increase of the ratio of SrS to CaS. The relative intensity for CaS is maximum whereas the relative intensity for SrS is minimum. There is only one band for all the samples in fluorescence as well as in phosphorescence.

This shift can be explained in terms of change in field strength due to change in lattice size as well as the effect of polarizability on the field strength. Initially, i.e. for the samples having up to 51.8 mol percentage of SrS in CaS, the effect of change in polarizability is predominant as compared to that of change in lattice size and leads to overall shift to longer wavelengths. However, once there is sufficient change in lattice size, its effect becomes predominant and since increase in lattice size leads to shift to shorter wavelength as against a shift to longer wavelength on account of the change in polarizability, the overall effect is to cause a shift to shorter wavelengths with further increase of SrS in CaS.
7.10 CORRELATION BETWEEN X-RAY AND EMISSION STUDY:

X-ray and emission studies reveal that there exists complete solid solution of CaS and SrS with each other. A single emission peak is obtained for these samples with some displacement of peak emission compared to individual emission peak in CaS : Cu and SrS : Cu as the concentration of the two sulphides is varied. There is not merely superposition effect of the two bands but a genuine shift. A change in lattice constant is also obtained. Thus one can say that the luminescence of mixed phosphors is modified by an exchange of calcium and strontium ions as solid solution is formed.

As mentioned already, there is a solubility limit for a solvent to form solid solution with any solute and beyond this limit excess solute will be precipitated. But in all the samples studied, complete solid solution exists over the whole range. There is also a regular variation of emission peak wavelength both in fluorescence and phosphorescence along with change in lattice size as can be clearly seen from figure 7.1 and Table II. The maximum shift to longer wavelength occurs at about 51.8 mole percentage of SrS both in fluorescence and phosphorescence. It is interesting to note that for this mole percentage of SrS, maximum deviation in lattice constant as compared to Vegard's law occurs.
FIG. 7.1 - GRAPH BETWEEN MOLE PERCENTAGE OF SrS & LATTICE CONSTANTS ALONGWITH PEAK POSITIONS OF FLUORESCENCE & PHOSPHORESCENCE.
7.11 ENERGY LEVELS OF THE EMISSION CENTRE:

As SrS is introduced in CaS, the band gap should decrease (the band gap of SrS being 4.8 eV and that of CaS being 5.4 eV). If the emission is explained on the Schon-Klasens model (figure 1.4), the shift in emission should be towards longer wavelengths such as has been reported in the case of ZnS : CdS mixed phosphors\(^{44,45}\). The shift can then be attributed partially to the change in the band gap and partially to the change in the crystal structure.

In the present case there is a shift first to longer wavelengths and then to shorter wavelengths in both fluorescence and phosphorescence emission. It is not explicable in terms of a change of band gap as well as a change of structure as it is not changing regularly with change in band gap and there is no evidence of change of structure.

The Schon-Klasens model in ZnS type phosphors assumes the emission to be due to an electron transition from the lower edge of the conduction band, or from a level very close to the edge, into a previously emptied level (due to Cu\(^+\)) not too far above the valence band edge. This model certainly does not apply to alkaline earth sulphide phosphors because (a) it would require independence of the spectra on the nature
of co-activators; (b) it would require the emission spectra simply to shift to lower energies (longer wavelengths) parallel to the change of the width of the band gap. Lehmann (loc. cit.) has studied the effect of the nature of co-activators and also the change in band gap in going from MgS to CaS to SrS to BaS in the copper activated phosphors of these alkaline earth sulphides. He has shown that both of the above predictions are in strong disagreement with the observations. The emission spectra do very definitely depend on the co-activator and there is no special shift over a range corresponding to the change in the band gap. These observations can only be understood on the basis of Prener-Williams type of recombination in which both the activator and co-activator are directly involved. Therefore it is worth while to describe the donor-acceptor theory proposed by Prener and Williams (46,47). According to this model, the electrostatic attraction results in the association of donor and acceptor levels which are perturbed towards their respective band edges due to this association (48). This theory has been applied by Crosnier and Curie (49) to explain the two bands emitted by ZnS : Cu phosphors. They have suggested that monovalent copper produces a localized acceptor level above the filled band. The radiative transitions originate from the bottom of the conduction band or rather from a shallow level related to a physical defect in the lattice to the acceptor level.
Comparison with emission characteristics of ZnS : Cu phosphors suggest levels due to Cu\(^+\) and S\(^{2-}\) vacancies. Taking into account the decay characteristics, thermal quenching and polarization properties, the emission spectra of ZnS : Cu phosphor were explained as due to transition from donor like S\(^{2-}\) vacancy level to an acceptor like Cu\(^+\) level. S\(^{2-}\) vacancies have been utilized to explain the self emission characteristics of CaS fired without activator by Ekbote\(^{(51)}\). This is explained as transitions between the acceptor like Cu level, a level little below the conduction band due to defects.

The shift first to longer wavelengths and later on to shorter wavelengths with increasing proportion of SrS in CaS can be explained in terms of the perturbations of the acceptor (Cu\(^+\)) and donor (S\(^{2-}\)) levels by the change in lattice size as well as changes in polarizability as explained earlier.

7.12 CONCLUSIONS:

The main conclusions drawn from the present investigations may be summarised as follows:

1. The decay of phosphorescence of all the samples of (CaS : SrS) : Cu phosphore has been found to obey the law, \(I = I_0 \cdot t^{-b}\), where 'b' is the decay constant.
(2) The value of decay constant for SrS phosphors is greater than that for CaS phosphors. This indicates the presence of shallow traps in SrS phosphors, which is in agreement with the fact that CaS phosphors in general show a long afterglow.

(3) The addition of SrS to CaS phosphors introduces shallow traps, thus reducing the time of afterglow.

(4) The hyperbolic decay could be explained on the basis of monomolecular superposition theory of Randall and Wilkins.

(5) The "peeling off" of the decay curves shows the existence of trapping levels, distributed probably in a quasi-uniform pattern. Trap depths obtained from decay studies reveal marked changes with increase in SrS concentration suggesting the introduction of new trapping states.

(6) The agreement between the values of trap depths calculated from the decay and glow curves justifies the use of Chen's theory of general order kinetics.

(7) The value of the pre-exponential factor 's' has been found to be of the order of $10^9$ sec$^{-1}$. The value of 's' goes on decreasing as SrS concentration increases.
(8) A change in the lattice constant of the mixed phosphor is obtained as the concentration of SrS increases in CaS. This may be due to an exchange of Ca and Sr ions.

(9) A substitutional solid solution of the two sulphides is formed over the entire range.

(10) Copper can occupy substitutional position in both the sulphides.

(11) A plausible model to explain the emission of the present phosphor system is Prener-Williams model with the perturbed Cu\(^+\), acceptor like level above the valence band and S\(^2-\) vacancy level near the bottom of the conduction band.
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