CHAPTER VI

Discussions and Conclusions

The results of decay and glow experiments are given in the third and fourth chapters, respectively and those of phosphorescence spectra in the fifth chapter. In this chapter the results are discussed and correlated and an attempt is made to arrive at certain conclusions.

1. Decay study:

(a) Flux and phosphor Composition

Samples without any flux do not luminesce. Phosphors having low concentration of flux show weak luminescence and short period afterglow. Similar observations are reported and discussed by Smith (1) and Wells (2). The optimum quantity of flux needed to produce efficient phosphors in the present investigations is 11.945% Na\textsubscript{2}SO\textsubscript{4}; 29.861% Sodium thio-sulphate (Hypo) and 2.996% NaF with respect to the CaS content. The optimum quantity of flux depends, of course, on firing temperature (3,4); firing time (5) and the atmosphere during firing (6,7). The present phosphors, on the basis of earlier trial, were prepared by firing in a reducing atmosphere at 900°C for two hours.

(b) Nature of the Decay Curves

Decay curves are in general hyperbolic as are seen from fig. (3.5) in chapter III. None of the decay curves on semi-log scale (log of intensity Vs. time) or
on log-log scale (log of intensity vs. log of time) as seen from figs. (3.6 & 3.7) is a straight line. The decay, therefore, cannot be represented by simple first or second order kinetics directly. The decay curves obtained on semi-log scale can be resolved into three exponentials, in general, by a peeling-off process. This shows that the decay consists of a superposition of exponentials and the hypothesis of superposition of exponentials suggested by Randall and Wilkins (8) is applicable for the decay of the phosphorescence intensity. Randall and Wilkins have ascribed the hyperbolic decay of the sulphide phosphors to electron traps of more than one depth, the hyperbolic form arising due to superposition of the different exponentials.

In the present investigations the decay curves are observed up to a period of about 40 or 45 minutes after the cessation of excitation. The nature of the decay is further investigated from the decay constant evaluated and the value of the correlation coefficient determined by decay observations. The correlation coefficient determined is nearly unity in almost all the samples (table 3.1). This increases the probability that these phosphors follow a power law.

The equation fitting in the present decay process may, therefore, be obtained by the hypothesis of superposition of exponentials. Considering the exponential decay corresponding to a single trap depth and assuming monomolecular kinetics,
Randall and Wilkins showed that the luminescence intensity at time 't' is given by

\[ I_t = I_0 \exp(-pt) \] \hspace{1cm} (6.1)

(Symbols having the usual meanings)

The above equation valid for a single trap-depth further assumes that retrapping is absent and that only radiative recombination between electron and hole take place. If there are \( N_E \) dE traps of depth between \( E \) and \( E + \text{d}E \), the phosphorescence decay for saturation conditions is given by

\[
I_t = \int_{E_{\text{min}}}^{E_{\text{max}}} N_E \exp\left(-\frac{E}{kT}\right) \exp\left[-st \exp\left(-\frac{E}{kT}\right)\right] \text{d}E
\] \hspace{1cm} (6.2)

The decay laws can be evaluated by assuming trap distribution as follows:-

(1) When the traps are uniformly distributed in depth i.e. \( N_E \) is constant, then the integration of (6.2) yields

\[ I_t = \frac{N_E kT}{t} \left\{ - \exp(-st) \right\} \hspace{1cm} (6.3) \]

For long time of decay (say more than a microsecond) it will reduce to

\[ I_t = \frac{N_E kT}{t} \hspace{1cm} (6.4) \]

This gives the information that luminescence intensity is inversely proportional to decay time.

(ii) If the distribution is exponential

\[ N_E = A \exp(-pE) \] as is found for many phosphors, then for \( st \gg 1 \), we get

\[ I_t = \text{const.} \cdot t^{-(p+k+1)} \hspace{1cm} (6.5) \]
where the constant \( p \) can be determined from the shape of the thermoluminescence curve and the decay itself follows a simple power law.

In the present investigations of CaS:Bi phosphors the decay was found to be of the form

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

where the constant \( b \) is 0.64, as given by the mean value of the decay constant, mentioned earlier.

Other important explanations of observed decay laws include those of Leverens (9) and Lehovec (10). Leverens has suggested that the form of decay curves is determined by the position of the activator site in the host lattice. The interstitial activator will give rise to power law decay and the substitutional to exponential decay.

Power law and exponential decay are explained on the basis of the relative concentration of positive and negative charges in the lattice. Despite its limitations Randall and Wilkins' theory is still generally accepted and it will also form the basis of interpretation of our results. A thorough examination of phosphorescence decay curves and thermal glow curves may be helpful in evaluating the effect of flux on trap distribution.

\((c)\) **Decay Constant**

Decay constant was estimated as described in Chapter III. The values obtained varied from 0.78 to 0.54.
The variation of decay constant with flux concentration is not regular/shown in fig. (3.8). The deviation of this constant from unity indicates that the trap distribution is not uniform (Equation 6.4) but is what may be called quasi-uniform. The deviation of decay constant indicates that either the trap depth changes or the distribution of traps in depth varies with the concentration of the flux. It is evident that the same phosphor has a greater decay constant when its initial intensity is higher. It suggests that as the number of filled traps increases, their mutual interaction will increase resulting in greater probability of escape for an electron from the trap and consequently decay constant will increase. It seems to be in accord with Wise's hypothesis (11) that as the concentration of filled traps increases the effective trap depth decreases.

(d) Trap depth by decay study

Trap depths by decay measurements are determined at room temperature with the help of the equation

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

and are tabulated in the table (3.2). The value of 's' in the present investigations has been taken of the order of \(10^9\) sec\(^{-1}\) as reported by Randall and Wilkins for alkaline earth sulphide phosphors (12). The decay curves are analysed into a series of exponentials by successive subtraction. It was found that at least three exponentials are required to account for the observed decay. 'p' is calculated from the slopes of the resolved exponentials. The trap depths obtained by decay observations are in good agreement with those determined by glow studies. The
variation of trap depth with flux concentration is, therefore, discussed in detail with thermal glow study. It is also inferred from values of trap depths that there is a single trap level in most all of the samples which is composed of a group of traps, which may probably be distributed in distinct but close sub-levels, as seem from fig (4.3).

The validity of the equation (6.6) related with the transition probability, is justified satisfactorily by indirect experimental evidence by the phosphors studied. A direct varification of this equation has been attempted by a number of workers (13-16).

2. Thermoluminescence Study

(a) Glow curves

Thermoluminescence studies were done at two different warming rates 0.430K/sec. and 0.230K/sec. and the results obtained by thermal glow study are tabulated in Chapter IV. A few phosphors show a double peak fig. (4.5'). From Randall and Wilkins' theory, the thermoluminescence glow intensity for single trap depth when heated with a uniform rate of \( \beta \), is given by the relation

\[
I = n_0 S \exp \left( -\frac{E}{kT} \right) \exp \left\{ -\int_0^T \frac{S}{\beta} \exp \left( -\frac{E}{kT} \right) dT \right\} \tag{6.7}
\]

where '\( n_0 \)' is the number of traps originally filled, 's' is the escape frequency, \( E \) is the thermal trap depth, \( T \) is the temperature and \( k \) is the Boltzmann constant.
From equation (6.7) it can be shown that trap depth $E$ is given by

$$E = k T_0 \log s \left[ 1 + f(s, \beta) \right] \quad (6.8)$$

where $T_0$ is the temperature of maximum glow and $f(s, \beta)$ is a correction term which is very small and is usually neglected.

In the above discussion Randall and Wilkins did not take into account the effect of retrapping. However, it is possible to discuss the effect of retrapping when the phosphor contains only traps of a single depth, but for more than one trap depth the effect becomes very complex.

The shape of the glow curves depends on the number of traps initially filled during excitation. When the deeper traps are not filled due to either low exciting intensities or low excitation times, variation in glow curves could take place due to retrapping by deeper traps of electrons freed from shallower traps. Garlick has pointed out that weak excitation is one of the favourable conditions for retrapping (16). Qualitatively it can, therefore, be concluded that retrapping plays a negligible role in the normal decay and the glow measurements in the present studies where the initial conditions were such as to ensure saturation of the filled traps. It is evident from the investigations of glow curves that the glow peak corresponding to higher rate of heating is sharper than that for lower rate of heating in
almost all the samples. The peak is further observed in accordance with theoretical prediction by Randall and Wilkins (3) to be shifted towards the higher temperature with the higher rate of warming. The samples with lower concentration of flux decay slowly and their peaks are broad, while the samples which contained optimum concentration of flux showed sharp maxima at the slower warming rate. Variation of intensity and trap depth observed in the study of glow curves indicates that the single trap level operative in a phosphor of this class constitutes a Gaussian group of traps in accordance with usual probability of distribution (3,17).

(b) Trap depth

Trap depths were calculated using the equation of Randall and Wilkins

\[ E = k T_g \log s \]  \[ (6.9) \]

where the correction factor \( f(s, \beta) \) in equation \( (6.8) \) has been neglected in comparison with unity. The value of \( s \) was taken of the order of \( 10^9 \text{sec}^{-1} \), which gives

\[ E = 21 k T_g \text{ (approx.)} \]  \[ (6.10) \]

Trap depths for the samples are determined with the peak temperatures corresponding to both heating rates used. The values of trap depths obtained for a sample from both warming rates are identical to a marked degree (tables 4.1 & 4.2). Trap depths corresponding to the single peak are plotted against the percentage of flux fig. (6.1).
Fig. (6.1) Trap depth Vs Flux
It shows that the trap depth does not change with the amount of flux added. However, in the case where NaF varies from 0 to 7.167% w.r.t. CaS, content the value of trap-depth is slightly less for lower concentration of NaF. As the flux content increases the number of deep traps evidently increases as can be seen from the gradual rise of the second peak. These observations indicate that variation of flux results in a slight change of operative trap-depth for different phosphors. Zhukova (18) has carried out investigations on the glow curves of Zns:Cu phosphors using halide fluxes and observed the merging into one another of the maxima in glow curves with increasing concentration of flux. The results similar to those of Zhukova have been observed in this case as well.

Most of the workers (19-21) in these laboratories has reported trap depth lying between 0.60 to 0.70 ev. in the case of CaS and SrS phosphors with different activators and fluxes (single and complex). This fact, along with the results obtained above, seems to indicate that the flux does not introduce in these phosphors any new trapping levels which are effective at room temperature. Zhukova has reported that the incorporation of fluxes does not create new lattice distortion, the flux atoms arrange themselves near the atoms of the activator.
3. **Correlation between decay and thermal glow curves**

There is a marked correlation between results of decay and thermal glow studies. Both indicate rise and fall of intensity and trap depth in almost a similar fashion, with variation of flux concentration. It is found that the trap depths calculated from thermal glow studies are in fairly good agreement with the trap depths corresponding to the middle exponential of decay analysis. The trap depth for a phosphor calculated from the glow curve is associated with the maximum of the Gaussian group of traps (22) being emptied at the peak temperature. Its counterpart evaluated by decay process at room temperature by the resolved exponential may not exactly correspond to the maximum of the operative group of traps. Then the glow trap depth is normally expected to be higher than that obtained by decay calculations for the same phosphor. This is in agreement with experimental observations (Tables 3.2 & 4.1). With a few exceptions, $E$ calculated from glow curves is always found comparatively slightly greater than that obtained by decay curves for the same sample. The two values of $E$ for a sample obtained by two peak temperatures (not much different from each other) corresponding to two different heating rates are found almost equal (Table 4.1 & 4.2) as may normally be anticipated. With these considerations both the studies show a complementary character. They seem to explain the nature of traps and
their distribution in the present phosphors supporting similar assumptions, including the probability of monomolecular kinetics being followed by these phosphor systems. Thus indirectly the application of the equation

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

appears to be justified in the case of these phosphors on the basis of the correlation obtained between the decay and thermal glow studies.

4. **Emission Spectra Study**

The results of emission spectra are given in table (5.1) Chapter V and are analysed here.

The CaS:Bi phosphors give only one emission band peaked at about 4473 Å. It is evident from the results that peak emission wavelength does not change with the amount of flux added. The emission intensity is found to increase with increase of flux concentration up to the optimum percentage beyond which it starts decreasing continuously. It appears that the fluxes up to the optimum percentages are useful for recrystallization and incorporation of the activator into the matrix lattice.

Figs. (6.2) show that when sodium sulphate was varied (Series -A) the changes in the maximum intensity were greater in comparison to those in which Sodium thiosulphate and Sodium fluoride were varied i.e. Series-B and Series-C, respectively. Once the optimum quantity of Sodium sulphate was fixed the changes in the intensity of
the samples due to variation of the other fluxes were less. These changes were minimum in Series-C in which the optimum quantities of Sodium sulphate and Sodium-thio sulphate were fixed. In this last series samples prepared at lower concentration of flux Sodium fluoride, show appreciable afterglow and maximum intensity occurs at 2.33% of Sodium fluoride with respect to CaS content and then starts decreasing to its minimum value at higher concentration of Sodium fluoride. Obviously, it quenches the luminescence at higher concentrations. These results indicate that Sodium sulphate is the most efficient flux and the least effective is Sodium fluoride. Sodium thio-sulphate has an intermediate efficiency.

The peak intensity may be assumed to be a function of the concentration of luminescence centres over a fixed area. Hence, fall in emission intensity for higher percentage of flux may mean that the number of luminescence centres over a given emitting area is reduced as the percentage of flux is increased above the optimum.

Fluorescence spectral studies of these phosphors were carried out by Saxena (23). He found that emission intensity increased with the increase of flux concentration only upto the optimum percentage beyond which it started decreasing continuously. He recorded the peak wavelength of fluorescence bands at about 4500 Å and there was no
change of peak wavelength with the concentration of flux, which is in good agreement with our results. He also reported on the basis of X-ray analysis that the lattice constant did not change with the percentage of flux.

As regards solid solution, the following conclusions were made by various workers. When the composition of a phosphor is altered by the formation of a solid solution with another compound, its emissive properties are likely to be altered (24). Leverenz has found that the addition of beryllium to zinc silicate activated with manganese serves to shift the colour of the emission to longer wavelength (25). This is due to the formation of a solid solution of the isomorphous zinc and beryllium silicates. A similar case is shown by the zinc cadmium sulphides. As the cadmium content is increased, the emission band of both the copper and silver activated phosphors is shifted continuously to longer wavelengths (26). Fired mixtures of calcium and strontium sulphides, activated with samarium have been studied by Rumpf (27). The position of corresponding lines in their diffraction patterns showed a linear change in lattice size within the range of 30 to 100 atomic percent strontium, denoting the formation of solid solutions. The position of samarium lines in the fluorescence spectrum showed likewise a continuous shift within this range.

But in the present phosphor system there is no change of peak wavelength and lattice constant with
the variation of the amount of flux and hence from these results it can be concluded that a solid solution is not formed.

5. **Activator Site in the Matrix lattice**

Activator concentration (12,23) needed to prepare efficient phosphors and the consideration of the size of the ionic radii (23,30) of the host crystal and the activator atoms help in drawing inference about the site of activator in the matrix lattice in a phosphor. The position occupied depends on the energy balance. The comparatively low activator concentration required to prepare efficient CaS:Bi phosphors in the present investigations, indicates the probability of bismuth occupying an interstitial position in the host lattice in the present phosphors. Decay process involved in a phosphor also assists in furnishing information about the activator site (31). The decay process in the present phosphors is observed to follow a power law. These considerations lead to the probability of interstitial incorporation of the activator in the matrix lattice in the case of the phosphor studied.

6. **Oxide Formation**

It is not out of place to remark about oxide formation in the present investigations. Oxide formation is an important factor in the study of emission spectra. The work carried out by Tunitskaya (32) has revealed the
importance of the presence of CaO in CaSiBi phosphors. Calcium oxide in a so-called 'pure' state has been extensively studied by Ewles (33). He found a very clear fine structure in the emission spectra with spacings attributed to vibrational frequencies of the ground state of the emission centre which he associated with the lattice cations. Addition of bismuth enhances certain groups of spectral lines and suppresses others. The theoretical analysis of the spectra of activated calcium oxide phosphors has been made by Runciman (34) with special reference to uranium, bismuth and samarium impurities.

The phosphorescence of the CaSiBi phosphors is blue in colour. Some 15 bands have been attributed to the bismuth activator in the CaS lattice and the data of different workers are often conflicting (32). The emission bands were found at 3900 A and 4500 A in unfluxed phosphors, but introduction of a suitable flux converted to CaO present to CaS and enhanced the 4500 A band and the 3900 A band was suppressed. It was interpreted that in the former case the lattice of CaO with a mixture CaS was formed and in the latter case the lattice of CaS was formed. CaO-Bi phosphor prepared under the same conditions was found to have the same properties as the phosphor with a base mixture of CaO + CaS.
In the present investigations, phosphors were prepared in a reducing atmosphere hence the chances of oxide formation were remote. Moreover, there is probability for oxide, if formed to be converted into sulphate or sulphide of calcium by reacting with Na₂SO₄ or Na₂S (likely to be produced by the reduction of some of the Na₂SO₄).

X-ray analysis does not reveal the presence of any line of CaO as reported by Saxena (23). This explains the presence of only one emission band in the present phosphors which can be attributed to bismuth in the lattice of CaS.

7. **Conclusions**

From the above discussions the following conclusions can be drawn:

(i) Phosphors prepared without flux do not show luminescence presumably due to lack of crystallization and difficulty in the incorporation of Bi⁺³ in the lattice.

(ii) For obtaining good emission characteristics there is an optimum concentration of fluxes, about 12% of Na₂SO₄, 30% of Sodium thio-sulphate and 3% of NaF are needed for the preparation of efficient phosphors.

(iii) Flux does not seem to introduce any new trapping levels operative at room temperature. These levels probably are associated with crystal defects and flux merely serves to alter their relative importance and not their mean depth.
(iv) Flux variation in a series indicates that at very low percentage of flux (from its optimum value) lower range of trap levels i.e. shallow traps of the group are operative, while at moderate flux contents, (optimum percentage range) the deeper traps of the group play a relatively important role.

(v) At lower flux percentage (below optimum) there appears to be want of fluxing material to distribute the activator atoms thoroughly enough in the matrix lattice. Consequently, shallow traps seem to be operative at lower flux contents.

(vi) The phosphorescence decay of these phosphors follows a power law of the form \( I = I_0 t^{-b} \), where \( b \) has a value of about 0.64.

(vii) The hyperbolic decay observed could be satisfactorily explained by a superposition of exponentials assuming monomolecular kinetics and no retrapping.

(viii) Equation \( p = s \exp(-E/kT) \) is found to be valid for application to these phosphor systems on the basis of the correlation obtained between the decay and thermal glow observations.

(ix) The phosphor system in the present investigations has a trap level of mean depth about 0.63±0.01ev.
(x) Bismuth in the lattice of CaS gives only one emission band peaked at about 4473 Å and it does not change its position with the variation of flux concentration.

(xi) Bismuth occupies an interstitial rather than a substitutional site in the matrix lattice.

(xii) There is no formation of solid solution in the present phosphor system.
8. References

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