CHAPTER V - DISCUSSION AND CONCLUSIONS.
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1. Theory of Concentration Quenching. If the concentration of activator in a phosphor is increased beyond a certain optimum value, the luminescence efficiency decreases. This phenomenon is known as concentration quenching. Various mechanisms are available for the explanation of this phenomenon. Some of the possible mechanisms are given below.

(1) Polymerisation Mechanism. This mechanism, first proposed by Walter (1) for luminescent organic solute, is related to the formation of pairs and higher aggregates of the luminophor molecules as their concentration is increased. These aggregates are assumed to be non-luminescent.

On similar reasonings, Ewles (2) attempted to explain the phenomenon of concentration quenching in inorganic phosphors by assuming Lenard's concept of luminescence centers. These centers are supposed to consist of an impurity atom or ion linked with a large number of host atoms, and are distributed randomly in the host lattice. He showed that the fraction of such centers for an atomic concentration $C$ of the activator to be $C / (1 + C)^n$, where $n$ is the number of host crystal ions associated with an activator atom. This expression reduces to $C \exp(-nC)$, if $C$ is very small.

Later, Ewles and Lee (3) extended the
theory by assuming that the activator will not function as luminescence center if perturbed by the overlap of another center. They deduced an expression, \( C = \frac{1}{n} \) for the evaluation of \( n \), the total number of lattice ions associated with the luminescence centers, from the experimental value of the optimum concentration of the activator \( C \). From this, the effective radius of the sphere of influence of the center can be estimated.

Johnson and Williams (4) also developed, independent of Ewle's work, a similar expression for the distribution of luminescence centers. They postulated that luminescence center is an activating atom or ion having no other activator atom or ion of the same kind within \( Z \) nearest lattice positions. They obtained an expression, \( C/(1-C)^Z \), for the fraction of activators functioning as luminescence centers. This expression is identical with that obtained by Ewles, provided \( C \) is small. The luminescence is quenched when any other activator happens to be within the \( Z \) lattice positions surrounding a given activator.

Thus the activator can not function as a luminescence center when within the range of influence of another activator ion. Since the fraction of activator ions within the sphere of influence of another activator ion increases with concentration of activator, the fluorescence yield must necessarily decrease at higher concentration of activators. In essence, concentration quenching is considered as equivalent to thermal quenching in the sense that the nearness of another activator
results in a substantial decrease in the thermal activation energy for promoting a non-radiative transition to the ground state.

(ii) Collisional Mechanism. This mechanism also, first applied to organic phosphors by Wawilow (6), assumes that diffusion-controlled collision between excited and unexcited luminophor molecules of the same species lead to a radiationless dissipation of absorbed energy. This type of collision is known as collision of the second kind. In such collision the electronic excitation energy is converted into kinetic energy of the interacting atoms, and the excitation energy is completely degraded into phonons. This is also a possible mechanism for concentration quenching observed in inorganic phosphors, as the number of interacting atoms increase at the higher concentration of activators.

(iii) Resonance Transfer of Energy. This mechanism was first suggested by Perrin (7) for the radiationless transfer of energy from an excited molecule to an unexcited one separated from the former by a large distance of the order of several angstroms in organic luminescent solutions. The theory was developed further by Förster (8) and applied to inorganic phosphors by Dexter (9) and Dexter and Schulman (10) to explain the mechanisms of sensitised luminescence and concentration quenching.

The resonance transfer of energy is
supposed to be the most plausible process in the sensitised luminescence of most of the inorganic phosphors when the activator has the forbidden nature of transitions but possesses excited states of energy almost equal to that of the excited states of the sensitizer. But as this process does not require the motion of the charges, and hence does not involve photoconductivity, its application has been confined mainly to the non-photoconducting phosphors. However, the possibility of such mechanism in photoconducting phosphors also has been indicated by Shionoya (11) and Shionoya and Asano (12).

Dexter and Schulman (10) assumed that degradation of energy takes place at special quenching sites which may be impurity atoms, vacancies, jogs at dislocation, normal lattice ions near dislocations or associated pairs or higher aggregates of activators. Quenching is assumed to involve the resonance transfer of energy from activator to activator until it arrives at an activator near one of the energy sinks. Finally, the activator quencher transfer occurs and the energy is lost.

(iv) Energy transfer through motion of charge. To explain the energy transfer from one activator to another of the same or different species, Mott and Gurney (13) has suggested this mechanism exclusively for photoconducting phosphors. In this mechanism as explained in Chapter I, hole in the valence band may be created
either by the direct excitation in the host crystal absorption band or by releasing it from the excited luminescence center. The hole then may be captured by a second activator and thus it is excited to receive electron from the conduction band, which is accomplished with the emission characteristic of the activator. Luminescence is quenched if this free hole is captured by some non-luminescent center.

(v) **Energy transfer through crystal lattice.** This mechanism involves both the charge transfer and the resonance transfer of energy and was advanced by Franck (14). The general assumption is that the positive holes are stabilised either in the activator atom or in the neighbourhood of an activator which always represents a point of lattice defect. When the electron is captured by the hole stabilised in the lattice defects, its potential energy is converted by internal conversion, into lattice vibrations and when the vibrational energy has dropped to a value equal to the excited energy of the activator, the energy is transferred to the activator which is then excited. If instead of the activators they happen to be quenching sites, the luminescence will be quenched.

(vi) **Cascade transfer of energy.** In phosphors having two different activators, the energy absorbed by one may be transferred to the other by cascade process provided that the first activator is reasonably
efficient and the second activator has a strong absorption band overlapping with the emission band of the first (5). In such cases, the short-wave emission band of the first activator cascade-excites the long-wave emission band of the second activator. However, luminescence will be quenched if the second activator forms non-luminescent centers by aggregation at the higher concentration of it.

2. Discussion.

(1) Suppression of the blue emission of \( \text{Bi activator} \) \( \frac{\text{Incorporation of}}{\text{very low}} \) concentration of Mn in CaS: Bi phosphor does not seem to have any marked effect on the fluorescence spectra of this phosphor. Because the intensities and the locations of the blue and orange emission bands of CaS: \((\text{Bi + Mn})\) phosphors do not show any appreciable change, except for some fluctuations in the intensities of the both, when the concentration of Mn is varied from 0 to \(1.116 \times 10^{-3}\%\). Above this concentration of Mn although the intensity of the blue fluorescence emission remains stationary, the intensity of the orange fluorescence first decreases sharply and then rises again slowly with the increasing concentration of Mn. This shows that the Mn activator is now effective, and the variation of the intensity of the orange band may be due to the interaction of the Mn and Bi centers responsible for that particular emission. The ineffectiveness of small proportion of Mn in CaS: \((\text{Bi + Mn})\) phosphors may be
due to the reason, as suggested by Bube (15) for the case of ZnS: Mn phosphors, that the effective luminescence centers are formed not from the isolated Mn ions, but from the pairs of them.

From the Mn concentration of $3.137 \times 10^{-3}$ %, the intensities of both the blue and orange emission bands decrease with increase in Mn concentration, but that of the orange decreases at a comparatively slower rate. The intensities fall down to a value of 20 from 100 for blue and to 40 from 83 for orange emission band at the Mn concentration of $9.460 \times 10^{-2}$ %. This shows the gradual influence of the Mn activator in re-enhancing the slowly decreasing orange fluorescence band due to Bi by producing its (Mn) own characteristic orange band. After that, the fluorescence intensity of the orange band rises continually and rapidly reaching a maximum value of 78.5 at the Mn concentration of $3.167 \times 10^{-1}$ %, whereas the intensity of the blue band after a slight rise falls down to 14.5 at the same concentration. Finally the blue fluorescence emission of Bi is completely suppressed at the Mn concentration of 1.035 %, but the orange fluorescence band of Mn persists. Visual estimation of the phosphorescence intensity also shows that the blue emission of Bi is gradually suppressed, while the orange emission of Mn becomes predominant above the Mn concentration of $1.256 \times 10^{-1}$ %.

So it seems that there has been an overlapping of Bi and Mn
centers as in the case of CaO : ( Bi + Pb ) phosphors where the suppression of Bi emission by the Pb activator was assumed \( (16) \) to be due to a transfer of energy from the excited Bi center to the Pb center. In the present case also, the suppression of both fluorescence and phosphorescence emissions characteristic of Bi with the subsequent enhancement of those of Mn suggests that the energy absorbed by the Bi centers is transferred to the Mn centers.

(ii) Quenching of the orange emission. The orange emission band of Mn does not show any increase in intensity with increase in concentration of Mn, after it has attained the maximum value at the concentration of \( 3.167 \times 10^{-1} \% \). Actually the intensity of the orange band should have increased in proportion to the decrease of the blue emission of Bi reaching a maximum value at the concentration of Mn corresponding to the complete suppression of the blue emission, because at this concentration maximum transference of energy from the excited Bi center to the Mn center would have been effected. But instead, the intensity of the orange band is found to decrease slowly with increasing concentration of Mn until it is finally quenched at the concentration of \( 4.711 \% \) of Mn. The phosphorescence glow observed just after the excitation also shows decrease in intensity with increase in concentration of Mn, and at the Mn concentrations of \( 4.174 \% \) and \( 4.711 \% \), it is hardly visible. Above that concentration of Mn, no glow is observed.
In view of the above results, it appears that the effective number of luminescence centers for orange emission is diminishing gradually due to the formation of competitive quenching centers. This is to be expected because the fraction of the luminescence centers within the range of other centers increase at the higher concentration of the activators. According to Schulman (17) such centers may absorb energy but they can not emit. So the formation of such centers may be the possible cause for the reduction of intensity of the orange emission at higher concentration of Mn, because a part of the energy transferred to such centers from the excited Bi centers is lost non-radiatively.

At very high concentration of Mn, there is every likelihood of the formation of pairs or higher aggregates of Mn centers. Dexter and Schulman (10) have pointed out that such aggregates act as quenching sites. Hence the quenching of orange fluorescence and phosphorescence at very high concentration of Mn may be explained as due to the transfer of energy from excited Bi centers to the higher aggregates of Mn centers.

The collisional mechanism, which also may cause quenching, can be rejected because direct analogue of such type of quenching has not been observed in solids (10).

(iii) **Mechanism of Energy transference.** In phosphors having two activators energy transference from one activator to the other of different
kind can be accounted for by any one of the four processes explained earlier under the theory of concentration quenching depending on the nature of the activators and the base material. However, the energy transference mechanism through the crystal lattice can be discarded as it involves the quadratic relation between the excitation energy and the subsequent yield of fluorescence emission, a relation which has not been found in practice (18, 19).

Energy transference by cascade process generally takes place when both the activators incorporated into the phosphor have allowed transitions as in Ag and Cu activated NaCl or ZnS phosphors (20, 21). In the present case the second activator Mn is known to have forbidden nature of transitions (19), and further CaS: Mn phosphor does not have any absorption band in the region at which the Bi emission occurs (14). Thus the Mn activator fails to fulfil the conditions required for the operation of the cascade process in CaS: (Bi + Mn) phosphors, and hence this process for the transfer of energy from excited Bi centers to the Mn centers can also be rejected.

Of the two remaining mechanisms both of which seem to be equally possible as CaS: Bi is a photoconducting phosphor (14), the resonance transfer mechanism is favoured in the present case over the charge transfer one on the following grounds.

(a) The suppression of Bi emission and the enhancement of Mn
emission at the higher concentration of Mn activator may be explained as due to the migration of holes from the excited Bi centers to the Mn centers and also due to the large cross-section of Mn centers for capturing the electrons from the conduction band. However, since the decay observed visually of the Mn emission is very short compared to that of Bi emission, the electrons released slowly from the traps must come to the ground state either non-radiatively by dropping into the non-luminescent centers formed by the higher aggregations of Mn centers or with the reappearance of Bi emission. At the particular concentration of Mn where its fluorescence and phosphorescence are maximum, the formation of non-luminescent centers of Mn ions by their higher aggregations seems incompatible. Hence, the Bi emission should have reappeared at the later stage of phosphorescence as in the case of CaS: (Cu + Mn) phosphors (14) in which the orange emission of Mn prevails first and then the green emission of Cu appears after the decay of the former. Since no such reappearance of Bi emission is observed in the present case, the occurrence of energy transfer mechanism through motion of charges in CaS: (Bi + Mn) phosphors appears doubtful.

(b) The forbidden nature of transitions involved in divalent Mn makes it necessary to be sensitized to give appreciable luminescence (12).

(c) In many inorganic phosphors, the Mn activator is effectively excited by resonance interaction with other impurity systems which
have been excited (18, 22).

(d) Divalent Mn as substitutional impurity in ZnS: Mn phosphor possesses deep lying levels which appear to be excited by resonance transfer of energy from the host crystal (15, 23).

(e) In ZnS: (Cu or Pb + Mn) phosphors also the Mn activator appears to be sensitized by the resonance transfer mechanism (11, 12).

Considering the close relationship that exists between ZnS and alkaline earth sulphide phosphors in most respects (14), it seems reasonable to assume, under the basis of the above given arguments, that resonance transfer of energy takes place in CaS: (Bi + Mn) phosphors also from excited Bi center to the Mn center.

(iv) Shift of emission bands. One of the criteria put forward by Leverenz (24) to determine the position of activators in phosphors is to find out the shift of the emission bands when the crystallinity of the phosphor is changed from low temperature to high temperature form. Shift of the peak position of the band to longer wavelength side indicates that the activator occupies the substitutional position in the crystal lattice of the phosphor, while the shift towards shorter wavelength side indicates the interstitial of the activator. This criteria may profitably be applied to the case of CaS: (Bi + Mn) phosphors in the present study. However, CaS phosphor is not known to have other allotropic forms. But
advantage may be taken of the Mn activator which enters into the crystal lattice substitutionally in many inorganic phosphors (25, 26, 27).

In the present case also, it may be assumed that the Mn activator enters into the CaS crystal substitutionally. In such cases the ligand anions surrounding a substitutionally located activator ion experiences a perturbation in proportion to the differences of sizes between the activator ion and the regular host crystal ion. Local distortion arises due to the contraction or expansion of crystal lattice according as the substitutional impurity is smaller or bigger in size than the host crystal ions. Thus the substitutional impurities may introduce more and more lattice abnormalities, change the nature of the base lattice and influence the optical properties of the system markedly when their proportion is increased (26). Local contraction of the crystal lattice of CaS will result when the Mn activator enters into it substitutionally as the ionic radius of Mn$^{+2}$ ion (0.91 Å) is smaller than that of Ca$^{+2}$ ion (1.06 Å).

The assumption that the Mn activators occupy substitutional positions in CaS: (Bi + Mn) phosphors is supported by the experimental results obtained in the present investigation that the orange emission band is shifted, although very slightly, towards longer wavelength with increasing proportion of Mn. The short afterglow of the orange emission of Mn
observed in the present case also favours the above assumption. Because it is generally believed (25) that very long afterglow lasting for hours is due to the interstitial positions of activators, while the shorter ones arise from the substitutional positions of them.

Now on the basis of the above considerations, the shift of the blue emission band characteristic of Bi activator towards shorter wavelength by about 100 Å may be attributed to the interstitial position of Bi in CaS: (Bi + Mn) phosphors. Further, the persistence of phosphorescence for about 12 hours observed in CaS: (Bi + Mn) phosphors with very low concentration of Mn or without it also indicates that the Bi activators occupy the interstitial position in the crystal lattice of the phosphors.

(v) Orange fluorescence band of CaS: Bi phosphor. The results presented in the last Chapter shows that Mn free CaS: Bi phosphor has two almost equally intense fluorescence bands located at 4500 Å and 5900 Å. This result is in conformity with Rothschild's report (28). He also observed two almost equally strong bands at 4500 Å and 5950 Å in CaS: Bi phosphor. On the other hand, Tunitskaya (29) found two emission bands at 390 mÅ and 450 mÅ in unfluxed CaS: Bi phosphors and only one band at 450 mÅ in the phosphor prepared with Na₂SO₄ as flux. X-ray diffraction studies carried out by her showed the presence of CaO with an admixture
of CaS in the phosphors prepared without flux, while the phosphors prepared with Na$_2$SO$_4$ as flux showed only the CaS lattice. On this basis she concluded that the emission band at 4500 $\AA$ was the only characteristic emission of CaS:Bi phosphors, and that the other band at 3900 $\AA$ was due to the presence of CaO:Bi phosphor which might have formed during the preparation of phosphor. This was supported by the observation of Ewles and Lee (3) who found the room temperature emission band of CaO:Bi phosphor peaking at about 3770 $\AA$. However, in the present case no such band has been observed although the sensitivity of the plate used for recording the fluorescence spectra of CaS:Bi phosphor extends to about 2750 $\AA$ in the shorter wavelength region. This confirms Tunitskaya's result that the origin of 3900 $\AA$ emission band due to the presence of CaO in CaS:Bi phosphor is suppressed by the use of Na$_2$SO$_4$ as flux, that is, oxide formation is reduced.

The orange emission band at 5900 $\AA$, observed in the fluorescence spectra of CaS:Bi phosphor in addition to the usual 4500 $\AA$ band, may arise due to the three possible causes given below.

(a) Alkaline earth sulphide phosphors prepared from their sulphates with Na$_2$SO$_4$ as flux may contain mixtures of sulphates, sulphides, poly-sulphides and complexes of metallic ion of the flux as pointed out by Wells (30). Kröger et al (31) have reported that rbdl. CaSO$_4$ or rbdl. SrSO$_4$ with Bi activator give
yellow, orange or red emissions of very short persistence. In view of their report, the orange emission band observed in CaS: Bi phosphor in the present investigation may be attributed to the presence of sulphate phase of the metallic calcium with the Bi activator.

(b) The orange emission in CaS: Bi phosphor may also arise from the direct recombination of the trapped electrons and free holes in the filled band. Such emission is called trap emission. This mechanism was proposed by Klasens (32), and is just the reverse process of directly filling up the traps by the excitation of electrons from the filled band as suggested by Riehl (33). The trap emission mechanism is supported by the experimental results that broad emission bands associated with the trivalent coactivators such as Sc, Ga and In have actually been observed (34) in ZnS phosphors. These coactivators are well-known for their properties of introducing trapping states in ZnS phosphors by giving rise to local perturbations in the conduction band (35). The theory of trap emission is further supported by the fact that the ions responsible for the deepest traps also produce the reddest emission. On this basis the Al coactivator which introduces shallow traps in ZnS phosphors should give an emission band in the short wavelength region. Indication of such band has indeed been found (32) in ZnS phosphors prepared with an excess of Al.

CaS: Bi phosphor is also known to have
a wide distribution of traps ranging in depth from 0.7 to 1.0 eV (36). So on the basis of the above arguments, the trap emission mechanism appears to be responsible for giving rise to the orange emission band in the fluorescence spectra of CaS: Bi phosphor. However, the trap emission mechanism does not seem to agree with the long period phosphorescence, lasting for about 12 hours, observed in CaS: Bi phosphor. Because the phosphorescence as well as the trap emission arise from the same trapped electrons, so if at all trap emission occurs the number of electrons in the traps should have reduced considerably thus shortening the period of phosphorescence appreciably. But no such abrupt end of phosphorescence has been observed in the present case. Hence the trap emission mechanism can be rejected as inadmissible in the present case for the origin of orange fluorescence band in CaS: Bi phosphor.

(c) The third possible cause is the host crystal emission. But Asano and Kishimoto (37) have shown that host crystal emission of CaS phosphors, containing Na$_2$S$_4$O$_4$ as flux and no activator, is located at 495 m$\mu$. However, in the present case, the 495 m$\mu$ band has not been observed, and the phosphors prepared without activators but containing Na$_2$SO$_4$ as flux do not show any glow. Hence the orange band observed in the present case may not be attributed to the host crystal emission.

Considering the above three possible causes, it appears that the presence of CaSO$_4$ or some other
impurities formed as a by-product during the preparation of the phosphor are responsible for giving rise to the orange emission band in CaS: Bi phosphors with very low concentration of Mn or without it.

3. Conclusions. From the studies of the fluorescence spectra of CaS: (Bi + Mn)\[Na_2SO_4\] phosphors and their phosphorescence, the following conclusions can be drawn.

(i) Introduction of very low concentration of Mn, from 0 to 1.116 \times 10^{-3} \%, in CaS: (Bi + Mn) phosphors does not produce any appreciable effect on the fluorescence and phosphorescence emissions produced by Bi activator alone.

(ii) The suppression of blue fluorescence and phosphorescence emissions characteristic of Bi and the enhancement of the orange emissions of Mn at higher concentration of it seems to be due to the transference of energy from the excited Bi center to the Mn center by resonance transfer process.

(iii) Quenching of the orange fluorescence and phosphorescence at very high concentration of Mn may be due to the formation of pairs or higher aggregates of Mn centers.

(iv) At higher concentration of Mn, the blue fluorescence band due to Bi shifts towards shorter wavelength side, while the orange fluorescence band due to Mn shifts towards longer wavelength side.

(v) Bi and Mn activators in CaS: (Bi + Mn) phosphors
appear to occupy the interstitial and the substitutional sites respectively in the host crystal lattice.

(vi) Orange fluorescence observed in CaS: Bi phosphor may be due to the presence of CaS\textsubscript{4} or other impurities formed as a by-product during the preparation of the phosphor.


| 28. | Quoted by Pringsheim, P. | "Dissertations" Jacob Van Campen, Amsterdam (1940). |

Ref. 14, Page 560.


