DISCUSSION

5.2 DISCUSSION :

The present study concerns with the luminescent behaviour of sodium bromide doped with heavy metal impurity, namely, thallous bromide and utilizes the available information to suggest physical models for the luminescence centres. Since valuable information regarding the fundamental processes that occur in alkali halides has been obtained by subjecting them to various pretreatments, the present study involves the measurement of excitation and emission spectra of untreated and variously pretreated NaBr:Tl phosphors differing in their thallium content.

The excitation bands observed in the present work, together with the emission bands excited by them, are discussed in certain groups depending on the convenience. In order to differentiate the luminescent features of undoped NaBr specimens from those of the doped specimens, initially the measurements were carried out on variously pretreated pure NaBr specimens. The results obtained in these measurements are presented first. Subsequently, the luminescent behaviour of thallium doped NaBr phosphors is considered. In the latter case the three emission band groups are catagorised on the basis of the spectral region in which they appear. The regionwise three groups of emission bands are those appearing in (i) ultraviolet, (ii) near ultraviolet, and (iii) visible region :

A) UNDOPED NaBr :

The emission exhibited by undoped sodium bromide is excited by absorption of light in the 264 - 276 nm region, (Figs.1a and 1b). The emission is observed at 360 nm as a dominant band in the spectra of all the undoped sodium bromide specimens subjected to heat and/or mechanical treatment, (Figs.2a and 2b). The data presented in Figs. 1 and 2 clearly indicate that the intensity of the excitation or emission band is dependent on i) whether the heat treatment offered to the specimen was in vacuum or in open air, and,on ii) the elevated temperature at which the specimen was annealed in open air and subsequently quenched. It has been observed that there is a marked increase in the intensity of the excitation or emission band if, instead of in vacuum, the specimen is heated in open air. Further, quenching of the specimen in open air from higher temperature enhances the growth of these bands. The maximum intensity for the excitation or emission band is obtained by heating the powder specimen in air to a temperature close to the melting point of NaBr (755°C) and then cooling it rapidly. In all the specimens, the intensity of 360 nm band decreases, if the specimen is deformed by stressing.

Many workers have proposed oxygen as a common impurity of most of the 'Pure' alkali halides, though, of course, little definitive work has been done with this impurity(124, 125). No absorption band has been found that can be clearly associated with oxygen. A yellow fluorescence observed by the excitation with ultraviolet light has been suggested to be due to O_2^+ impurity(126). Etzel(127) suggested the absorption centres connected with oxygen in additively coloured alkali halide crystals containing hydroxyl ion impurity. In the measurement of the spectral distribution of the emitted light in the thermoluminescence of undoped NaCl Halperin <u>et</u> <u>al</u>.(128) observed a prominent band around 360 nm . Examination of the luminescence or thermoluminescence spectra of undoped NaCl specimens by other workers(129-131) also revealed a dominant emission band at about 360 nm . As suggested by Halperin et al(128), a process involving the diffusion of oxygen and positive ion vacancies during heat pretreatment of the specimens is responsible for their luminescence.

It is, therefore, tentatively concluded that the heat treated undoped NaBr specimens acquire the property of becoming luminescent because the surface of the microcrystal (in the powder specimen) gets activated due to the adsorbed oxygen. On this basis one can say that at a particular temperature the attack of oxygen molecules on the surface layers will naturally depend on the availability of oxyten. This is supported by the fact that there is a considerable difference in the luminescence intensity of the emission band at 360 nm for the two specimens, one heated in vacuum and the other in air (Fig. 2a) , though both were annealed at 500°C for the same duration. Further, with the rise in temperature the probability for the adsorbed oxygen molecules to enter the microcrystal lattice will increase. Hence one would expect maximum luminescence intensity for the specimens heated in air at temperature near its melting point.

It is suggested that the oxygen molecule-ion O_2^+, which is one of the components of the luminescence centre responsible for 360 nm emission, occupy cation site in the perfect region of the lattice. Comparison of the excitation and emission spectra displayed by undoped NaBr specimen, annealed and quenched from 500°C in vacuum and a doped NaBr specimen (Tl Conc. $\sim 10^{-4}$ m.f.) also annealed and quenched from 500°C in vacuum (Fig. 4) reveal that the introduction of a trace amount of thallium impurity completely supresses the intensity of the 360 nm band. This may be because of the fact that the Tl^+ ions entering the lattice take substitutional position in the NaBr lattice thereby reducing the available number of vacant cation sites and giving characteristic Tl emission which overshadows, the 360 nm emission attributed to oxygen emission centres.

It may be noted that in the emission spectra of thermally pretreated (in air) and subsequently deformed specimens, a subsidiary band at 432 nm appears and simultaneously, there is a decrease in the intensity of the emission at 360 nm (Fig. 2b). The reason for this could be that some of the 360 nm centres in the perfect region are converted to 432 nm centres due to distortion. Thus, 432 nm centres may be 360 nm centres in the strained region of the lattice.

B) THALLIUM DOPED NaBr :

i) ULTRAVIOLET EMISSION :

It has been observed in the present investigation that in the emission spectra of the NaBr:Tl specimens in as-received condition the emission band at 328 nm appears quite prominent at lowest Tl concentaration ($\sim 10^{-4}$ m.f.), but its strength diminishes as the Tl concentration is increased (Figs. 4 and 6). The intensity of this band also decreases if the specimen is examined after compression to tablet, (Fig.8).

In this respect the behaviour of 328 nm emission band is analogous to that of 305 nm emission band observed in KCl:Tl phosphors. The 328 nm emission exhibited by NaBr:Tl phosphors, is favoured mainly by the excitation at 268 nm, (Figs. 3, 5 and 7). In analogy with the 247 nm absorption and its corresponding 305 nm emission in the spectra of KCl:Tl phosphor which have been explained satisfactorily on the basis of Seitz - Williams theory , it is proposed that the 268 nm excitation and the 328 nm emission in NaBr:Tl arises in isolated Tl^+ ions occupying Na^+ ion positions in the perfect region of the lattice. In other words ultraviolet emission is the property of the crystallinity of the lattice. The 268 nm excitation can then be due to $^1S_0 \longrightarrow {}^3P_1$ electronic transition within an isolated substitutional Tl^+ ions and the 328 nm emission can be ascribed to the inverse electronic transition $^3P_1 \longrightarrow {}^1S_0$.

In the emission spectra for the specimens annealed and quenched from higher temperature (Figs. 10 and 12), the 328 nm band appears quite prominent for the lowest two concentrations. This is because a thermal treatment would provide uniform distribution of isolated Tl^+ ions in the bulk of the specimen. For the higher Tl concentration, the band in the ultraviolet is completely erased (Fig. 26) . One may therefore conclude that at higher Tl concentration two or more Tl^+ ions occupy nearest neighbour positions and thereby cause quenching of emission in the ultraviolet region.

From the emission spectra of annealed and slowly cooled specimens (Figs. 14 and 16) it is inferred that the solubility of Tl in NaBr is quite high (to be discussed in section (iii)a). Hence at lower Tl concentration ($\sim 10^{-3}$ m.f.) most of the thallium is retained in solid solution by the host lattice even after the specimen is subjected to slow cooling treatment. The emission spectra of annealed and slowly cooled specimens with two lower Tl concentrations ($\sim 10^{-4}$ and 10^{-3} m.f.) also show dominant band in the ultraviolet (Fig. 14). Slow cooling should bring about aggregation of Tl^+ ions in the lattice but because the concentration of Tl is low, such an effect is not significant. Hence one would expect in this case Tl^+ ions in dispersed state in the lattice. This naturally results in exhibiting prominent ultraviolet emission. At higher Tl concentration the aggregation of Tl^+ ions will be significant which leads to the destruction of isolated Tl^+ ions and hence the supression of ultraviolet emission.

When any of the untreated or thermally treated specimen is subjected to compression, the dislocation density in the specimen will increase due to dislocation motion and dislocation multiplication. The crystallinity of the lattice will therefore be disturbed . As a result of this, a fraction of the isolated Tl^+ ions will either condense on the dislocation or find itself in the dislocation region thereby giving rise to another species of Tl centres. Thus the decrease in the intensity of the 328 nm peak after compression can be understood (Figs. 8, 12 and 16).

The excitation band at 268 nm mainly favours emission at 328 nm . There is another subsidiary excitation band at 220 nm , which is also observed to give the same ultraviolet emission though weaker in intensity. Thus two excitations namely, 228 and 268 nm favour one emission. The reason for this could be that the radiation at 228 nm is more energetic and hence its excites the Tl^+ ion to a higher energy state from where it drops to the lower state (emission level) corresponding to the 268 nm excitation. Thus in both the cases the transition takes place from the lower excited state and hence only one emission band is observed corresponding to the two excitations.

ii) NEAR ULTRAVIOLET EMISSION :

In the case of NaBr:Tl phosphor the emission in the near ultraviolet region (between 360 - 390 nm) is favoured by two excitation bands. The maxima of these bands vary between 238 - 242 nm and 270 - 276 nm .

The study of the excitation spectra of TlBr - -powder reveals that the excitation spectrum is quite broad and diffused one reaching from 220 to 280 nm (Fig. 36, Curve : 1). Irradiation of the TlBr - powder specimen with light belonging to any of the wavelengths between 220 and 280 nm gives rise to emission only in the near ultraviolet region (360 nm band), (Fig. 37, Curve : 1). TlBr - powder specimen after compression also shows the emission in the 360 nm band, (Fig. 37, Curve : 2). The corresponding excitation band varies between 220 - 280 nm (Fig. 36, Curve : 2).

Investigation of the excitation spectra of aqueous TlBr - solution indicates that in this case the maximum of excitation band varies between 220 and 234 nm depending on the concentration of the solution. The increase in the concentration of the solution leads to shift of the excitation band to long wavelength side (Fig. 38). The corresponding emission has its maximum lying between 360 - 370 nm . In this case also with the increase in concentration of the TlBr - solution, the emission band shifts to long wavelength side. Fig. 39 indicates that the intensity of the emission of TlBr - - solution increases with the decrease of TlBr concentration and reaches a maximum for an optimum concentration (dilution ratio 1;5). With further dilution, the intensity of the emission band begins to drop. This is because of the fact that in a solution the degree of dissociation of the molecules into ions decreases with the increase in concentration of the compound(132). The number of TlBr molecules and Tl^+ ions existing in equilibrium in solution depend on the TlBr concentration in the solution. At higher concentration, one would expect the molar concentration of undissociated TlBr - -molecules to be very much greater than the concentration of the Tl^+ ions formed by the dissociation of the molecules. It is suggested that in a concentrated TlBr - - solution the excited TlBr - molecule may be strongly perturbed by the interaction with a nearby unexcited TlBr molecule. In such a case an internal conversion can be made probable which will inhibit the eventual fluorescence emission of the absorbed energy. On this basis the existence of the optimum concentration can be explained. When an excited TlBr - molecule is certain distance apart from an unexcited TlBr - molecule, the quenching probability of the former by the latter is minimum. Dilution of the TlBr - solution beyond optimum concentration leads to further decrease in the concentration of TlBr - molecules and an increase in the concentration of Tl^+ ions. Thus the main excitation band and the corresponding emission band in TlBr - solution, observed under varying TlBr concentration, seem to arise from electronic transitions within TlBr-molecule.

Comparing the results of the excitation and emission spectra of TlBr - powder, aqueous TlBr - solution with those of the solid NaBr:Tl phosphor as-received from solution, (Table 3), it is observed that the positions of the maxima of the excitation and emission bands in the above three systems are roughly the same. Hence one may assume that in all the three systems the excitation and emission originate from internal electronic transitions within the same kind of centre namely, TlBr - molecule. It may be noted that in the case of TlBr - solution the near ultraviolet emission is observed by excitation in the band around 225 nm . In the case of solid NaBr:Tl phosphor there are two excitation bands, around 240 and 273 nm . Out of these two, the excitation at 273 nm gives rise to strong emission in the near ultraviolet region. However, since the emission behaviour with respect to 240 and 273 nm excitations is more or less similar, both these bands have their origin in the same kind of centre i.e. TlBr - molecule (in two different excited states).

It is proposed that a substitutional Tl^+ ion in the distorted region of the lattice forms one of the components of the centre responsible for near ultraviolet emission of the NaBr:Tl solid phosphor. In the distorted region of the lattice, Tl^+ ion will not occupy a position of cubic symmetry. Because of the local lack of cubic symmetry there is a significant possibility that a Tl^+ ion in the distorted region forms a covalent band with one of the neighbouring Br^- ion(133) . This would form a TlBr - molecule with an axis in the < 100> direction.

One can now conveniently explain the origin of the emission bands in the near ultraviolet region, when the Tl concentration in NaBr is increased beyond 10^{-3} m.f. in the case of all the untreated or pretreated NaBr:Tl solid phosphor. Because of the higher thallium concentration it is presumed that there are localised strains (or static distortions) in the lattice which provide environment conducive to the formation of TlBr - molecule.

It is observed that at higher Tl concentration there is an overall decrease in the intensity of the near ultraviolet emission and simultaneously one observes an increase in the intensity of the bands in the visible region when the specimens are subjected to pressure, (Figs. 22 and 24). This is because of the fact that the compression of the specimen induces dislocation multiplication and hence a significant number of Tl^+ ions finds itself in the dislocation region. As mentioned later, Tl^+ ions in the dislocation region are presumed to form complex ions of the type $(TlBr_n)^-$ which are supposed to be responsible for emission in the visible region.

It is observed that when the specimen (Tl concentration more than 10^{-3} m.f.) is subjected to annealing at 500°C and subsequent quenching to room temperature, the near ultraviolet emission appears as a shoulder on the emission band in the visible at 420 nm (Fig. 26 , Curves : 1 and 2). As may be expected, annealing and rapid cooling will give rise to uniform distribution of Tl^+ ions in the bulk of the host lattice. Since the Tl concentration is high, statistically there is a significant possibility for two Tl^+ ions to occupy nearest - neighbour positions in the lattice thereby giving rise to the characteristic visible emission at 420 nm as discussed later..

In the case of annealed and slowly cooled specimen, the near ultraviolet emission is significant when the Tl concentration is $\sim 10^{-2}$ m.f. . When the Tl concentration is increased to 10^{-1} m.f. , the near ultraviolet emission is overshadowed by the emission in the visible at 420 nm (Fig. 30, Curves : 1 and 2). Slow cooling will in general, favour aggregation of impurity as a result of which Tl^+ ions in the NaBr lattice at high thallium concentration will come nearer each other and form Tl^+ centres in nature different from those responsible for near ultraviolet emission.

The emission in the near ultraviolet region is mainly between 360 - 370 nm .. It has been observed that in some cases the maximum in the near ultraviolet region shifts to even 350 nm. This is attributed to the predominance of the ultraviolet emission band which has an extensive overlap on the near ultraviolet

TABLE : 3 :

Coincidence of the Excitation and Emission Bands of Solid NaBr:Tl Phosphor, TlBr - Powder and TlBr - Solution .

(Wavelength in nm)

Sr. No.	Specimen	Maximum of excitation band	Maximum of emission band
	NaBr:Tl powder phosphor prepared from solution		
1.	Tl Conc. $\sim 10^{-2}$ m.f.	M 242 (17)	S 378 (18)
		S 270 (17)	S 364 (18)
2.	Tl Conc. $\sim 10^{-1}$ m.f.	M 240 (19)	S 380 (20)
		S 270 (19)	S 366 (20)

Contd...

		Maximum	
Sr. No.	Specimen	of excitation band	of emission band
3.	NaBr:Tl powder phosphor prepared from solution and then pressed to tablet. Tl Conc. $\sim 10^{-2}$ m.f.	M 242 (21)	M 386 (22)
		S 270 (21)	S 366 (22)
4.	Tl Conc. $\sim 10^{-1}$ m.f.	M 242 (23)	M 370 (24)
		S 272 (23)	S 366 (24)
5.	TlBr-powder in as-received condition.	Broad excitation band reaching from 220 - 280 nm with poorly resolved maxima. (36)	Strong emission band at 360 nm. (37)
6.	TlBr-powder pressed to tablet.	" (36)	" (37)
7.	Aqueous TlBr-solution	Maximum appears between 220 and 234 nm depending on TlBr-Conc. (38)	Maximum appears between 360 and 370 nm depending on TlBr-Conc. (39)

band and consequently the peak position of the near ultraviolet emission shifts to shorter wavelength . Similarly predominance of visible emission has the effect of displacing the peak position of the near ultraviolet emission to longer wavelength (towards 390 nm). One may therefore conclude that the peak position of the near ultraviolet emission band depends on the variation in the intensity of the overlapping ultraviolet or visible emission.

iii) VISIBLE EMISSION :

The excitation spectra of heavily doped NaBr:Tl phosphor clearly show that the excitation bands for such phosphor favouring visible emission appear in the region between 244 - 250 nm and 274 - 280 nm , (Figs. 33 - 35). It should be noted that the excitation maximum for near ultraviolet emission appears anywhere between 270 nm and 276 nm whereas excitation maximum for visible emission occurs between 274 nm and 280 nm. Thus there is significant overlap between the excitation bands for near ultraviolet emission and the excitation bands for visible emission. The corresponding emission spectra exhibit bands mainly around 420, 450, 480 and 500 nm. In what follows the physical models of the centres associated with these emission bands are discussed.

a) <u>420 nm emission</u> :

It is observed that the band around 420 nm appears in the emission spectra of most of the specimens as-received from solution when Tl concentration is high. At high thallium concentration, the Tl^+ ions occupying Na^+ ion positions in the lattice will be more numerous in number and hence there is a significant possibility for two Tl^+ ions to occupy nearest neighbour positions. It can therefore be reasonably assumed that the band at 420 nm has its origin in Tl^+ ion pairs (dimers).

Specimen annealed and quenched from 500°C (in vacuum) will have a significant fraction of Tl^+ ions in solid solution involved in the formation of dimers. This is because in annealed and quenched specimen the number of Tl^+ ions in the substitutional positions will be large and at the same time these ions will be uniformly distributed in the volume of the specimen.

When the isolated Tl^+ ions are thickly populated there will be considerable probability for two Tl^+ ions to occupy nearest neighbour positions and form dimers. This should make 420 nm peak more prominent compared to the neighbouring peaks on the lower and higher wavelength side (Fig. 26). One can therefore understand why 420 nm band is prominent in the spectra of annealed and quenched specimen compared to that in specimen as-received from solution (Figs. 18 and 20, Curve : 1).

In the case of the specimen annealed and slowly cooled from 500°C (in vacuum) the condition of higher concentration of Tl^+ ions in solid solution is also presumed to have been satisfied . On this basis the prominence of 420 nm band in the emission spectra of this specimen can be well explained (Fig. 30, Curve : 2). The presumption is based on the following information namely, the arrangement of ions in an alkali halide crystal depends on the relative sizes of the ions(134). When the radius ratio $R_M:R_X$, where M stands for the metal ion and X for the halide ion, is smaller than a certain limiting value, the space available for the central positive ion inside a lattice will be greater.

The ionic radius of $Cl^- < Br^- < I^-$. Thus when Tl^+ ion occupies a substitutional position in sodium halides, the empty space available around the substitutional Tl^+ ion in NaCl , NaBr and NaI lattices will increase in that order. In other words, the solubility of Tl will be highest in NaI, lowest in NaCl and in between the two in NaBr. This is in accord with the reported experimental results namely, dimers are observed in NaI:Tl(115, 116) but are not observed in NaCl:Tl(135). The retention of Tl in solid solution in NaBr after slow cooling can therefore be reasonably assumed even at higher Tl concentration.

When the untreated or pretreated specimens at high Tl concentration (more than 10^{-3} m.f.) are subjected to compression, the 420 nm peak is, in general, supressed. The effect is more significant for the specimen as-received from solution or for slowly cooled specimen. However, it is not so significant in the case of annealed and quenched specimen, (Figs. 22, 24, 28 and 32). It is suggested that dislocation motion and their consequential multiplication will be more marked in the case of the specimen obtained either by crystallisation from solution or by slow cooling. This is anticipated because due to nonuniform distribution of Tl^+ ions in such specimens the dislocation motion will, in general, be less obstructed by isolated Tl^+ ions or their aggregates acting as pinning sites for dislocations. Increase in dislocation density due to dislocation motion will create different environment for Tl centres in the lattice and hence the 420 nm emission decreases after deformation.

In the case of annealed and quenched specimen Tl^+ ions will be widely dispersed in the volume of the crystal. Such ions will be significantly responsible in making the dislocation motion impossible by elastic interaction. Thus the locking points in the specimen being more numerous in number, there will not be any increase in its dislocation density. This could be the reason why the strength of the 420 nm band is not much affected by deformation.

b) 450 and 480 nm emissions :

The study of the excitation and emission spectra for saturated NaBr - solution containing varying amounts of TlBr reveals that the emission of such an aqueous solution appears around 460 nm. A subsidiary emission around 480 nm is also discernible, though weak in intensity, for optimum TlBr concentration. The results are given in Figs. 40 and 41 and in tabular form in Table (5). It may be noted that the excitation of the 460 nm emission can be caused by absorption of light in the 250 as well as in the 280 nm band.

Comparison of the data presented in Table (4) for solid NaBr:Tl phosphor with that given in Table (5) for saturated NaBr - solution containing TlBr indicates close parallelism in their behaviour. For instance, in both the cases there are two excitation bands out of which the principal one appears around 280 nm and the subsidiary about 250 nm . Similarly in both the cases the emission is around 450 and 480 nm.

There is sufficient evidence that complex ions of the type ($TlBr_n$)$^-$ exist in solution. Scott and his co-workers(136-138) have determined the dissociation constants and molar absorptivities of TlCl, ($TlCl_2$)$^-$,

TABLE : 4 :

Excitation Bands for Visible Emission Exhibited by As-received and Variously Pretreated Solid NaBr:Tl Phosphor.

(Wavelength in nm)

Sr. No.	Specimen	Tl Conc. in m.f.	Fig. No.	Excitation band	Emission band for which the excitation is observed
1.	NaBr:Tl powder phosphor as-received from solution and then pressed to tablet.	10^{-1}	34	248 276	450 450
2.	NaBr:Tl powder phosphor annealed and quenched from 500°C and then pressed to tablet.	10^{-1}	34	248 274	450 450, 480
3.	NaBr:Tl powder phosphor annealed and slowly cooled from 500°C and then pressed to tablet.	10^{-1}	34	250 274 280	450, 480 450 480

TABLE : 5 :

Excitation and Emission Bands Exhibited by Saturated NaBr - Solution Containing Varying Amounts of TlBr .

(Wavelengths in nm)

Sr. NO.	Specimen	Excitation band/ bands	Emission band/ bands
1	Saturated NaBr - solution + 1 drop of TlBr-solution	270 (40; Curve:1)	460 (41; Curve:1)
2	Saturated NaBr - solution + 2 drops of TlBr-solution	276 (40; Curve:2)	460 (41; Curve:2)
3	Saturated NaBr - solution + 3 drops of TlBr-solution	264; 280 (40; Curve:3)	460 (41; Curve:3)
4	Saturated NaBr - solution + 5 drops of TlBr-solution	250; 284 (40; Curve:4)	460; 480 (41; Curve:4)
5	Saturated NaBr - solution + 6 drops of TlBr-solution	250; 284 (40; Curve:5)	460; 480 (41; Curve:5)
6	Saturated NaBr - Solution + 7 drops of TlBr-solution	250; 286 (40; Curve:6)	460; 480 (41; Curve:6)

TlBr, $(TlBr_2)^-$ and $(TlBr_3)^-$. The luminescence spectra of KCl - TlCl and KBr - TlBr solutions have also been studied by various authors(139-141) which indicate that the charged complexes of the type $(TlX_n)^-$ (where X denotes the halide) exist in solution. Study of the absorption spectra of aqueous solutions of thallous halides led Fromherz et al(142, 143) to believe that complex ions of the type $(TlCl_n)^-$, existing in aqueous KCl:Tl solution, also exist in solid KCl:Tl phosphor and these ions are the centres of luminescence in solid phosphor. The complex ion model for the luminescence centre in solid phosphor was also supported by Pringscheim(144) and Hilsch(145). However, this model was relegated in the background soon after Seitz (1938) published his substitutional thallous ion model for the luminescence centres in thallium doped alkali halides. Later on it was observed that substitutional ion model was not adequate to explain all the features arising in solid KCl:Tl phosphor(22, 23). Results obtained by Ewles and Joshi(146) (Proc. Roy. Soc. 1960) provided evidence sufficient to conclude that the absorption bands observed in aqueous KCl-TlCl solution are additionally observed in the spectra of solid KCl:Tl phosphor if its thallium content is high. Thus besides substitutional Tl^+ ions one also expected complex ions of the type $(TlCl_n)^-$ to act as luminescence centres in solid KCl:Tl phosphor.

From the identical behaviour of solid NaBr:Tl phosphor and NaBr - TlBr solution, as evident from tables 4 and 5, it would be reasonable to attribute the 450 and 480 nm emissions in the case of solid NaBr:Tl phosphor to the complex ion centres. It is known that at any given temperature certain optimum concentration of the activator can go in solid solution with the host material. Hence the excess Tl will precipitate with the passage of time if its concentration exceeds the equilibrium solubility in NaBr lattice. In the case of NaBr:Tl phosphor the Tl^+ ion (radius 1.44 A°) is much greater in size than Na^+ ion (radius 0.95 A°). In this case the precipitation effect should become significant to reduce the strain energy of the crystal. In alkali halides such precipitation effects have been recorded before in the direct observation of 'decorated' dislocations(147 - 150).

In heavily doped NaBr:Tl specimen the excess

Tl^+ ions would precipitate along the dislocations present in the crystal. The precipitation effect depends on the dislocation density in the crystal. Near the core of an edge dislocation in an alkali halide crystal, one can visualise halogen ions which do not have proper number of nearest neighbour alkali ions. The bromine ions which do not have identical environments, may possess different degrees of association with the nearest neighbour Tl^+ ion precipitated on the dislocation core. It is suggested that the Tl^+ ions precipitated along the dislocation lines are complexed with certain number of Br^- ions to form different species of aggregates of the type $(TlBr_n)^-$. Transitions in such complex ions are presumed to be responsible for the emission at 450 and 480 nm. On the basis of their stability one may argue that the comparatively stronger 450 nm emission be attributed to lower complex ions and the weaker 480 nm emission to the higher complex ions. The above given hypothesis is well substantiated by the fact that the emission bands at 450 and 480 nm are comparatively more pronounced when the specimen is deformed by stressing.

In such a specimen, the dislocation density would increase after deformation creating thereby environment conducive to the formation of complex ion centres.

c) 500 nm emission :

The excitation and emission spectra of NaBr doped TlBr (TlBr:Na) phosphor is represented in Figs. 42 and 43 . The excitation spectra of the phosphor exhibit bands about 250 and 280 nm (Fig. 42 ; Curve : C) . The emission data, for TlBr:Na phosphor clearly demonstrates that with the increase of NaBr content of the phosphor, there is a quenching of the characteristic near ultraviolet emission of TlBr and enhancement in the intensity of the emission bands in the visible region. The increase in NaBr concentration mainly favours emission around 500 nm region (Fig. 43, compare Curves : 1 & 2).

The emission around 500 nm has also been observed in some of the NaBr:Tl specimens at higher Tl concentration (Fig. 26, Curves : 1 and 2 ; Fig. 30 , Curve : 2). Similarly the corresponding excitation spectra exhibit bands around 250 and 280 nm (Fig. 35).

From the parallelism observed in the preferential emission at 500 nm for excitation with wavelengths either at 250 or at 280 nm in the case of NaBr:Tl and TlBr:Na phosphors it is suggested that in the two systems, the excitation and emission arise in the same kind of centre namely, Na^+ ion occupying Tl^+ ion position in TlBr lattice .

Thus in the case of NaBr:Tl phosphor at high thallium concentration there appears a possibility of Na^+ ions entering TlBr lattice substitutionally. The TlBr in the phosphor is supposed to have precipitated out as a separate phase due to higher excess of Tl above its equilibrium solubility at room temperature. The substitutional Na^+ ion centres in TlBr are responsible for emission at 500 nm.