C O N C L U S I O N S

425 nm band. Further, the excitation of the emission in the visible region can be caused by absorption of light in the 230 as well as 260 nm region.

Comparison of the data presented in Table 4 for solid NaCl:Tl phosphor with that given in Table 5 for saturated NaCl-solution containing TlCl indicates close parallelism in their behaviour. For instance, in both the cases there are two excitation bands out of which the principal one appears in the 260 nm region and the subsidiary in the 230 nm region. Further, the maximum of the principal excitation band in both the cases shifts to longer wavelength with the increase of Tl concentration.

The absorption spectra of simpler complex ions, formed by the association of cations and anions in pairs or other simple small groups, have been extensively studied. Evidence that complex ions of the type $(TlCl_n)^-$ exist in solution is manifold. Scott and his co-workers[83,84,85] have determined the dissociation constants and molar absorptivities for TlCl, $(TlCl_2)^-$, TlBr, $(TlBr_2)^-$ and $(TlBr_3)^-$. The luminescence spectra of KCl-TlCl and KBr-TlBr solutions have also been studied by various

authors[86,87,88] which indicate that 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 with alkali halides led Fromherz et al.[89,90] 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 Pringsheim[91] and Hilsch[92]. 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[18,19]. Results obtained by Ewles and Joshi[68] (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 might also expect complex ions of the type $(TlCl_n)^-$ to act as luminescence centres in solid KCl:Tl phosphor.

From the identical behaviour of solid NaCl:Tl phosphor and NaCl-TlCl solution, as evident from Tables 4 and 5, it would be reasonable to attribute the visible emission in the case of solid NaCl:Tl phosphor to the complex ion centres. It is known that at any given temperature say, room temperature, certain optimum concentration of the dopant 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 NaCl lattice. In the case of NaCl:Tl phosphor the Tl^+ ion (radius 1.44 Å) is much greater in size than Na^+ ion (radius 0.95 Å). In this case the precipitation effect should become all the more 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[93,94,95,96]. In untreated and heavily doped NaCl:Tl specimens the excess Tl^+ ions would precipitate along the dislocations inherently present in the crystal. In the thermally and/or mechanically pretreated specimens the precipitation effect would be accelerated due to increase in the dislocation density of the crystal. Near the core of an edge dislocation in the

crystal of an alkali halide, one can visualise halogen ions which do not have proper number of nearest neighbour alkali ions. The chlorine ions, which do not have identical environments, may possess different degrees of association with the nearest neighbour Tl^+ ion precipitated on the core. It is suggested that the Tl^+ ions precipitated along the dislocation lines are complexed with certain number of Cl^- ions to form different species of aggregates of the $(TlCl_n)^-$ type. Transitions in such complex ions are presumed to be responsible for the emission in the visible region. The present hypothesis can adequately explain the increase in the strength of the visible emission with the increase in Tl concentration and due to thermal and/or mechanical treatment of the phosphor.

From the results of the present investigations the following conclusions can be drawn:

(1) It is clear from the present measurements that the properties of NaCl:Tl system and KCl:Tl system are not identical. They differ significantly in their details.

(2) The 320 nm emission, exhibited by lightly-doped NaCl:Tl phosphor is favoured by excitation into 256 nm band. As in KCl:Tl system, this luminescent characteristic is attributed to an isolated substitutional Tl^+ ion in the perfect region of lattice.

(3) The results of the excitation and emission spectra for solid NaCl:Tl phosphor, TlCl powder and aqueous TlCl-solution exhibit similarity in their luminescent behaviour. The positions of the maxima of the excitation bands in the three systems are roughly the same whereas the emission region (360-390 nm) for these systems exactly coincide. Hence

it seems plausible to assume that in all the three systems the excitation and emission originate from internal electronic transitions within the same kind of Tl centre namely, TlCl molecule.

(4) It is observed that the emission in the visible region for solid NaCl:Tl phosphor becomes significant with the increase of Tl concentration and for a given concentration of Tl the intensity of the emission is enhanced if the phosphor is subjected to thermal and/or mechanical treatment.

Comparison of the data for solid NaCl:Tl phosphor with that for saturated NaCl-solution, containing varying amounts of TlCl, indicates close parallelism with respect to their excitation and emission behaviour. For instance, in both ~~the~~ cases there are two excitation bands out of which the principal one appears in the 260 nm region and the subsidiary in the 230 nm region. Further, the maximum of the principal excitation band in both ~~the~~ cases shifts to longer wavelength with the increase of Tl concentration. These

excitation bands are observed for emission in the visible region.

From identical behaviour of solid NaCl:Tl phosphor and aqueous NaCl:TlCl solution, it would be reasonable to attribute the visible emission in the case of solid NaCl:Tl phosphor to the complex ion centres. It is suggested that the Tl^+ ions precipitated along the dislocation lines are complexed with certain number of Cl^- ions to form different species of aggregates of $(TlCl_n)^-$ type. Transitions in such complex ions are presumed to be responsible for the emission in the visible region. The present hypothesis very well explains the increase in the strength of the visible emission with the increase in Tl concentration and due to thermal and/or mechanical treatment of the phosphor.

(5) Most significant difference in the behaviour of KCl:Tl and NaCl:Tl system is that the visible emission for heavily-doped KCl:Tl system is attributed to dimer (i.e. Tl^+ ions in pairs)

since the strength of the absorption bands responsible for this emission varies as the square of thallium concentration. On the other hand, the intensities of the visible emission bands exhibited by NaCl:Tl system do not show dependence on thallium concentration which can be ascribed to dimer. In fact at higher thallium concentration, because of the large size of Tl^+ ion compared to Na^+ ion, most of the thallium impurity precipitates at dislocation sites and gives rise to complex ions.