CHAPTER III

SPECTRAL CHARACTERISTICS OF PHOSPHORS

3.1 PHOSPHOR :

Phosphors are crystalline insulating materials capable of absorbing energy from various sources and re-emitting as visible or near visible radiation during or after excitation. Phosphors are very sensitive to structural changes and impurities and as such, they are strongly influenced by chemical composition, crystal structure, impurities present in relatively small amounts and physical conditions, e.g. temperature and type of excitation under which they are made to luminesce. The main components of a phosphor are (i) Host matrix (ii) Activator (iii) Flux.

(i) HOST - MATRIX :

The pure insulating crystalline material forms the base or host which primarily functions as a suspension for activator or imperfections and also as an energy transfer medium which surrounds the activator atoms. It promotes luminescence by favourably altering the energy levels under the perturbing influence of the activator so that storage and radiative transitions are possible. The chemical composition of the host material should be such that it should have a high melting point and also relatively high solubility for foreign cations or anions or both.

(ii) ACTIVATOR :

An element or ion which gives rise to localized energy levels in the forbidden gap of an insulator or semiconductor and which permit radiative transitions is called activator. Depending on the nature of its function, an activator can be classified as originative, intensifier, co-activator, sensitizer and killer. Originative activator gives rise to new emission lines or bands other than the intrinsic luminescence of the host lattice, if any. Intensifier activator intensifies the intrinsic luminescence of the host lattice. Coactivator can produce a luminescence having the same properties as those of the activators. It is indispensable for the formation of luminescence centres together with activators but the emission wavelengths are dominated only be the species of the activators. An activator is known as a sensitizer if the energy absorbed by it is transferred to another activator without radiative emission.

Killer activator gives rise to energy levels to which radiative transitions are forbidden.

(iii) FLUX :

The precise action of the flux is as an agent that promotes low temperature crystallization of the phosphor which would otherwise decompose when heated upto the melting point. Prevalent views regarding its role in phosphor synthesis and the mechanism by which they affect luminescence characterstics are : (1) It acts as a mineralizer and a catalyst which allows lower firing temperature and shorter firing time by promoting low temperature recrystallization so rapidly that large grains with lattice imperfections are formed. (2) It acts as an inhibitor of sublimation. (3) It promotes even distribution and incorporation of activator in the host lattice. (4) It promotes the formation of defects or lattice distortions and thus affect the luminescence efficiency. (5) Flux atoms arrange themselves around the activator atoms and thus increases the effeciency of phosphors. (6) It provides charge compensating ions when ionic charge of the activator differs from that of the host lattice ion ;

it replaces and facilitates the entry of such activator, probably because charge compensation by this way is less costly in energy than by the formation of vacancies and interstitials..

3.2 EXCITATION SPECTRUM :

Every luminescence process consists essentially of three parts : the absorption or excitation, the emission (both practically instantaneous) and interposed between them, the storage of the excitation energy, which determines the average duration of the luminescence. In the measurement of the excitation spectrum, the total emission is measured as a function of the wavelength of the exciting light. Excitation is intimately connected with absorption. It is, of course, axiomatic that a phosphor must absorb those photons which excite it, but it does not follow that all absorbed photons excite photoluminescence, even when the energy of the primary photon is greater than that of the emitted photon. In many cases, there is a fairly strong absorption commencing at a certain (ill - defined) wavelength λ_0, but excitation of detectable photoluminescence does not occur until the wavelength of the primary photon is made considerably smaller than λ_0. In such a case, the energy of absorbed primary photons is converted into heat, or something other than photoluminescence. The excitation spectra of phosphors, therefore, do not necessarily coincide with their absorption spectra, although luminescence is generally excited by photons whose energies lie in or near the region of strong host-crystal absorption. While every excitation band must be an absorption band, the intensity distribution in the two spectra can be different because the luminescence yield need not be the same for the various absorption mechanisms and some absorption bands may even be missing from the excitation spectrum. Moreover, the excitations spectra for fluorescence and phosphorescence can be different.

In general, absorbed monochromatic radiation with wavelengths shorter than the host crystal absorption edge will excite luminescence, although the efficiency of excitation often falls to very low values in the soft X-ray region. When excitation occurs, and when the phosphor has a single (simple) emission band, the entire luminescence emission band is produced, regardless of the wavelength of the primary excitations. The shapes and locations of single emission bands of phosphors are practically independent of the energy of the individual excitant particles, it being assumed that the intensity of excitation is insufficient to increase the temperature of the phosphor appreciably(78).

Primary photons with different energies often excite fluorescence (during excitation) and phosphorescence (after excitation) emission of different degrees, depending on the energy of the excitant photon. Certain phosphors which exhibit fluorescence and appreciable visible phosphorescence under one excitant may exhibit only fluorescence, with very little visible phosphorescence, under another excitant. Whenever phosphorescence is observed after excitation, however, fluorescence is always observed during excitation.

The constitution of the host crystal and the nature of the activator centre are both important in determining the excitation spectra of phosphors. The bands corresponding to the excitation of long-lasting phosphorescence are connected, in general, with lattice defects, while light absorbed in the absorption bands of the non-perturbed base lattice gives rise to an afterglow of shorter duration; only fluorescence is produced when light is absorbed by electronic transitions in the atoms or ions of the activating metal.

3.3 EMISSION SPECTRUM :

Emission spectrum gives the luminescence intensity as a function of wavelength of the emitted radiation. The study of the excitation and emission spectra of a phosphor is important not only from the theoretical point of view as far as it provides internal information about the activator levels and the crystalline field to which the activator ion is subjected in the host crystal, but also from a practical point of view of developing luminescent materials for specific applications. Luminescent emission involves optical transitions between electronic states characteristic of the radiating substance. The emission spectrum for many substances is, therefore, independent of the nature of the excitation and we obtain, for example, in cathodoluminescence, the same emission bands as in photoluminescence. However, more detailed examination reveals definite shifts in the position of these bands, especially at high excitation densities(79).

The emission spectrum of a phosphor, in general, consists of one or more bands, which are characteristic of not the activator alone, but of the combination of the activator and base material. The bands can have peak wavelength anywhere between ultraviolet to infra-red region(80,81), the position being attributed to activators. The energy jumps for a given transition are not exactly the same throughout the volume of the phosphor, hence the emission spectrum of a phosphor is not confined to a narrow line but is spread on either side of the most probable transition producing a relatively broad and continuous set of wavelengths.

The emission bands have usually symmetrical intensity distribution which is well represented by a Guassian curve(82-83). In some cases, bands seem to be complex and can be analysed by superposition of several bell-shaped curves, which may be ascribed to the superposition of lattice oscillations on a simple electronic frequency or to the superposition of several electronic transitions(84,85). Luminescence of most inorganic solids involves impurities or structural defects (e.g. vacancies) and in some cases co-activators as well. These imperfections are of diverse atomic or molecular types (complex centres) whose characteristics depend on the nature and structure of the imperfection and on the electronic states of the perfect crystal. The electronic states involved in luminescence due to impurities can be approximate, in some cases, in terms of the energy levels of the impurity ion perturbed by the crystal field and in other cases, in terms of the band structure of the perfect crystal perturbed by the impurity.

The electronic states originating from impurities and structural defects and responsible for luminescent emission contribute to the optical absorption bands on the long wavelength side of the fundamental absorption edge of a perfect crystal. The luminescent emission in most cases lies at an even longer wavelength. In other words, the luminescent emission lies in spectral region where the crystal is non-absorbing. This is one of the most striking features of luminescent emission that it occurs for most substances in the spectral region where the crystal is transparent. Besides the electronic states of the perfect crystal or of the activator involved, other electronics states of the activator of the other impurities or imperfections may contribute to the efficiency of, and time constant for, luminescent emission. Non-radiative de-excitation either within the activator or at other defects may compete with the radiative de-excitation. Metastable states of the activator and electron or hole traps arising from defects spatially removed from the activator, delay the luminescent emission and are thus responsible for phosphorescence. Because thermal activation of metastable levels or traps is a prerequisite to emission, phosphorescence is strongly temperature dependent. During continuous excitation both fluorescence and phosphorescence mechanisms contribute to luminescent emission in proportions depending on the steady state kinetics of these processes.

3.4 HISTORICAL REVIEW

a) INTRINSIC LUMINESCENCE OF ALKALI HALIDES :

It was found that the compounds KCl, KBr, NaCl show relatively feeble luminescence in the pure state at room temperature. When the temperature is lowered below the boiling point of liquid nitrogen (77°K), these compounds luminesce in the pure state with very high efficiency. A weak luminescence has been studied by Timusk(4) at 300°K. The study of the emission spectra of these compounds have also been made at 12°K, when excited with ultraviolet light.

In order to investigate the nature of the centre responsible for the intrinsic luminescence of the alkali halides, two experiments have been perfound. First of all, it was shown by Weeks and Teegarden(9) that exposure to UV-light at 93°K produced F or F' bands in the alkali halides. Their irradiation in these bands gave rise to emission identical with the intrinsic luminescence. This indicates that the luminescence is due to the recombination of electrons with trapped holes, either by tunneling from an excited state of the electron trap or by electrons reaching the trapped hole via the conduction band. Presumably, the electron is captured in an excited state about the trapped hole and luminescence occurs when the hole and electron recombin. Edgerton(10) suggested that the hole involved in this process might be self-trapped, rather than trapped at a defect. Subsequent investigations of this recombination luminescence by Kabler(86), Murray and Keller(87) have established the fact that the hole trap involved in the intrinsic luminescence of KI and RbI is indeed a V_k - centre or self-trapped hole (Castner and Kanzig(88)). This work was done principally on crystals X-rayed at low temperatures to produce F-centres and V_k-centres directly. The emission bands obtained were found to be similar to, but not identical with those obtained by excitation with ultraviolet light. The optical properties of the V_k-centre have been studied by Delbecq and Co-workers(89), and by Hersh(90). The centre is caused by covalent bonding between two neighbouring negative ions, one of which has lost an electron.

Edgerton(10) studied excitation spectra for each of the emission bands observed in RbI at 80°K. The short wavelength emission band is most efficiently excited by energies higher than the peak of the first exciton band, while the low energy band is preferentially excited in the long-wavelength tail of the first exciton band. Weeks and Teegarden(9) measured an excitation spectrum for the total luminescence of a KI crystal. This spectrum differs from that of RbI, in that all the radiation from the KI crystal was incident on the detector, whereas the radiation from the RbI was dispersed by a monochromator, to select one or the other of the emission bands. All the excitation spectra exhibit strong minima at the peak of the first exciton bands in these compounds. It is interesting to note that while minima occur also at the positions of the higher energy absorption bands, they are not nearly as pronounced. The emission spectra of RbI and KI single crystals have been measured at 12°K by Ramamurti and Teegarden(7). A typical spectrum of excitation at 205 nm in RbI was studied. Although bands analogous to those occuring at 80°K are observed at the lower temperature, others also appear, which are not resolved or are quenched.

Studies of recombination luminescence in other alkali halides have also been made and tentative assignments of observed emission bands to molecular transitions have been made. Some of these assignments have been partially verified by polarization studies.

b) LUMINESCENCES OF Tl DOPED ALKALI HALIDES :

Thallium doped alkali halide phosphors have evoked considerable interest of a fundamental nature for the past thirty years. The Tl^+ - ion have outer electronic configuration S^2. The introduction of Tl^+ - ions have a pronounced effect upon the optical properties of the alkali halides. When Tl^+- ion is substituted for an alkali ion, several new absorption bands arise. Extensive bibliography related to the work on thallium doped alkali halides is given by Curie(1).

One typically observes a similarity in the absorption spectra of all alkali halides upon introduction of thallium into them. Three principal absorption bands are observed which are lebelled by Seitz(3) as A, B and C bands. The A and C bands are strong and rather temperature independent, whereas the strength of the weaker B-band is temperature dependent. The spectral positions of these bands in KCl:Tl are 247, 206 and 195 nm respectively, with the relative strength as $C > A > B$. The principal emission band at 305 nm and a weaker emission band at 475 nm were attributed to the 247 nm and the 195 nm absorption bands respectively.

Seitz(3) was the first to present a detailed theoretical analysis of experimental work on many different impurities in the alkali halides. His analysis was based upon the positions of the energy levels of free thallous ion states, and upon expected modification of these levels when the ion was in a crystal. The details of his model and its modification by Williams are given below :

The information available about KCl:Tl phosphor when Seitz gave his model was that it has one absorption band peaking at 247 nm and two overlapping bands with peaks at 195 nm and 206 nm . There are two possible mechanisms which could be responsible for these absorption bands.
(i) In pure alkali halide crystals it was shown by Hilsch and Pohl(91-93), Schneider and O'Bryan(94) that this absorption band could be due to the transition of an electron from a halide ion to an adjecent alkali ion. The work required to shift an electron to a thallous ion from a neighbouring halide ion will be less because of the higher ionization potential of thallium than that of any alkali metal. Such transitions will therefore

give absorption lines on the long-wavelength side of the fundamental absorption of KCl. (ii) The second alternative is that whole of the absorption is due to the thallous ion itself. Seitz favoured the second alternative. The reasons for such an assumption are as follows :

(a) There is a characteristic pattern of the three absorption peaks in the case of all the alkali halides activated with thallium. The positions of these peaks shift only slightly as the alkali or halogen ions are changed.

(b) No potoconductivity is excited in the KCl:Tl phosphor simultaneously with the phosphoresence. This indicates that the excited electron is not raised into a free conduction band but is retained within the sphere of attraction of the Tl^+ - ion.

(c) The peaks shows none of the doublet structure which Hilsch and Pohl(91-93) have associated with the doublet state of the halogen atom.

(d) There is a very small temperature dependence of the peak positions of the absorption and emission bands.

From this data Seitz concluded that the

luminescence centres were thallous ions replacing the alkali metal ions of the crystal lattice. When a thallous ion replaces an alkali metal ion in the crystal, its energy level will be modified by crystalline interaction. Seitz attempted an evaluation of this modified energy level scheme on the following lines :

In the unexcited state the interaction of the thallous ion with the lattice consists of electrostatic attraction and homopolar repulsion (negative Van der Waals forces). In the first excited state the excited electron is shared by the adjecent ions and the charge distribution is not the same as for the excited thallous ion in the free state. In this excited state the electrostatic attraction remains the same as in the normal state but the interaction between closed shell configuration of electrons is different. This causes the energy levels of the excited states to be depressed relative to those of free ions.

Taking these factors into account, Seitz arrived at a disposition of levels in KCl:Tl crystals. The configuration of the ground state of the Tl^{+}- ion is $6S^{2}$and the ground state is $^{1}S_{o}$. That is, the spins of the two electrons are anti-parallel. It is known from the spectroscopic studies of the free Tl^+- ion that the lower excited states arise from the configuration 6S6p and consists in order of increasing energy of ${}^3P^o_o$, ${}^3P^o_1$, ${}^3P^o_2$ and ${}^1P^o_1$ states. Transitions ${}^1S_o \longrightarrow {}^3P_1$ and ${}^1S_o \longrightarrow {}^1P_1$ are allowed, their relative intensities depending upon the size of the spin - orbit splitting. Seitz identified the two strong absorption bands 247 nm and 195 nm with the two most probable transitions ${}^1S_o \longrightarrow {}^3P_1$ and ${}^1S_o \longrightarrow {}^1P_1$ respectively. Transitions ${}^1S_o \longrightarrow {}^3P_2$ are forbidden in the atom, but suggested that lattice vibrations might make them weakly allowed in the crystal, he assigned the B band to them. This suggestion is consistent with the strong temperature dependence of the B-band(95). According to him, if the cubic symmetry of the crystal arround thellous ion is perfect, then other transitions are forbidden, but local lack of symmetry may cause one or more of them to be present in absorption. The absorption band 206 nm was thus assumed to be such transitions.

A semiempirical approach to the task of computing these levels was taken by Williams(12). He attempted to show that the significant luminescent properties of KCl:Tl phosphor can be derived quantitatively from theory and calculated the energy of ^1S_o and $^3P_1$ states of the Tl^+-ion in KCl from first principles and the properties of the constituent ions. The terms considered were those arising from the Madelung, repulsive, Van der Waals, ion dipole and coulomb overlap forces. The energies of these two states were computed as functions of the distance between the thallium ion and its nearest neighbours chlorine ions so that quantitative configuration coordinate curves were obtained. From these curves it is possible to compute the peak positions and the temperature dependence of the band widths of the 247 nm absorption and 305 nm emission bands corresponding to $^1S_o \rightleftarrows {}^3P_1$ transitions. Further, it is indirectly concluded that from selection rules the second allowed transition $^1S_o \rightleftarrows {}^1P_1$ accounts for the 195 nm absorption and the 475 nm emission. From absorption and emission data, it is also possible to compute the configurational coordinate curves for simple systems(96). Johnson and Williams(20) suggested a similar scheme. They proposed a configuration coordinate curve for $^1P_1$ state using experimental data as a base. In addition, to account for the observed trapping effect, they proposed tentative coordinate curves for the ^3P_o and $^3P_2$ states.

On the basis of previous experimental work, the role of electron transfer states in the electronic structure of Tl^+ - ion centre in KCl:Tl system was re-examined by Knox(14). He concluded that the importance of such states may be greater than the previously thought, especially in a quantitative explanation of oscillator strengths and the spin orbit interaction responsible for the separation between the A and C bands. According to Knox, the appearance of additional absorption bands at higher energy than the C-band can also be attributed to electron transfer states. Furthermore, later experimental work has revealed structure in the absorption bands of the thallous ion centre and analogous bands of isoelectric impurities, such as Sn^{++} ion, which indicate that the centre due to these impurites may not be as symmetric as previously thought. This idea is borne out by the discovery that the luminescence of many of these centres can be polarized.

c) SINGLE THALLOUS ION (MONOMER) ABSORPTION :

Seitz(3) suggested that the band at lowest energy, namely 247 nm band, corresponds to the transition

${}^1S_o \longrightarrow {}^3P_1$ and the strong band at highest energy, namely 195 nm band, to the transition ${}^1S_o \longrightarrow {}^1P_1$. The small band lying between them was attributed to the transition ${}^1S_o \longrightarrow {}^3P_2$, partially allowed because of vibrational perturbations.

Another feature of interest in the Tl^+ ion absorption is the existence of structure in the A and C bands. For example, Yuster and Delbecq(95) carried out the measurements of $KI:Tl^+$ at 77°K and discovered that the C-band (${}^1P_1$) actually consists of three components at lower temperature. They suggested that this splitting might be due to a removal of the threshold degeneracy of the ${}^1P_1$ state by thermal vibrations, although such an effect would also be expected to split the ${}^3P_1$ band, which remains single according to their experiments. They also discovered a new absorption band in KI:Tl labelled D (226 nm) along with the three absorption bands labelled A (283 nm), B (245 nm) and C (234 nm) . The D - band in KI:Tl lies between the C - band and onset of the fundamental absorption of the crystal. This band which has since been discovered in KCl:Tl by Kuwabara and Aoyogi(97) is at too low energy to be due to higher lying states of the thallous ion. Yaster and Delbecq(95) suggested that this band is analogous to the α and β bands which appear in the alkali halides, i.e. due to the transitions on anions which surround the Tl^+ - ion. Knox(14) suggested that the D-band is due to a charge transfer state involving a transition from an anion to the Tl^+ - ion.

The study of the absorption spectrum of KCl:Tl at many different concentrations of Tl^+ ions at both room temperature and at 77°K was made by Wagner(98) . His work bears out the discovery of Patterson(23) that both the A and C bands are not single. The C-band shows a triplet structure analogous to that observed in KI:Tl. The A-band has two components and possibly three. These structures exist in other thallium phosphors and even more pronounced in Pb^{++} and Sn^{++} phosphors (Fukuda(16) and Zazubovich <u>et al</u>(99), Wagner(98)). The cause of this splitting is not completely clear, although a number of proposals have been made to explain it. These proposals fall into three catagories. (1) Local asymmetry due to the presence of other charged ions or vacancies nearby; this was suggested by Zazubovich et al(99) to explain results on Sn^{++} and could be important for Pb^{++} as well;

(2) Asymmetry due to a static distortion in the otherwise perfect lattice that removes the cubic symmetry ; and (3) Dynamical Jahn - Teller effect. Recently Delbecq et al(100) studied the trapping and annihilation of electrons and holes in KCl:Tl systems. In an associated absorption study they obtained number of absorption bands which they attributed to the presence of Tl^{+}, Tl^{++} and Tl^{o} centres. The absorptions at 247, 209 and 195 nm have been identified as the well-known A, B and C bands (Seitz's terminology) respectively. The bands at 380, 250, 300, 640, 1260 and 1500 nm have been attributed by these authors to Tl^{o} atoms and the bands at 220, 262, 294 and 364 nm have been ascribed to Tl^{++} ions.

The study of the properties of NaI:Tl system reveals that in the case of isolated Tl^{+}- ion in NaI one observes the usual A, B and C absorption bands located at 292 nm, 248 nm , and 234 nm respectively at 17°K (Vaidanich(101)). The A and C bands show structure. There appears to exist a D-band ~ 230 nm which is very close to the fundamental absorption. Apparently the excitation spectrum in NaI (Tl) is rather similar (qualitatively) to that of KI:Tl and the same sort of arguments regarding its origin might apply. Although NaI is deliquesent and therefore requires special experimental percautions, the usefulness of NaI(Tl) as a high energy particle detector (Hofstadter(102)) had led to further study of its properties (Van sciver and Hofstadter(103); Van Sciver(6,104,105) ; Eby and Jentschke(106) ; Herb and Van Sciver(107) ; Vaidanich(101) ; Herb(108)).

d) SINGLE THALLOUS ION (MONOMER) EMISSION :

Until recently the absorption spectra of the thallium doped alkali halides received more attention than the details of the emission spectra. For example, prior to 1959 it was believed that the emission spectra were independent of excitation energy and that in many of the alkali halides only one emission band appeared. In fact there are typically serveral emission bands whose intensities, polarizations and lifetimes are dependent upon temperature and the wavelength and the polarization of the exciting light. Although several schemes have been advanced to explain these phenomena, a complete understanding has not yet been reached. The recent work by Edgerton and Teegarden(15, 109) has resulted principally in the discovery of many more emission bands at higher photon energies than those known at the time of Seitz's contribution. They studied the emission spectrum of KI:Tl for three different temperatures. (1) At room temperature, excitation in A, B or C bands produces a broad emission peaking at 413 nm. (2) At 80°K, excitation in the A - Band yields an emission at 430 nm, whereas excitation in the B and C bands produces this emission along with one at 305 nm. (3) At 12°K these two bands are joined by three new ones.

Excitation in the A - bands yields intense emission at 336 nm and weak emission at 430 nm, B - band absorption is followed by emission at 287 and 336 nm, C - band absorption yields 279 nm, 336 nm, 305 nm, and 430 nm emissions and absorptions in the D - band yield intense emission at 430 nm and 336 nm.

Edgerton and Teegraden(109) have suggested that each of the five observed emission bands correspond to one of the five excited states of the thallous ion centre. The 413 nm emission comes from the $^3P_0$ state, the 336 nm emission from $^3P_1$, the 305 nm from one of the $^3P_2$ states (split in the cubic field), the 287 nm from the other of the $^3P_2$ states and the 279 nm from $^1P_1$ state. The appearance and disappearance of these bands as a function of temperature could be interpreted in terms of radiationless transitions, for example, at 300°K excitation into any band would be followed by a radiationless transition to $^3P_0$, from which 413 nm emission arises. Also, certain of the emissions seem to involve the reabsorption of emitted radiation, followed by lower energy emission. For example, radiation emitted at 279 nm could be reabsorbed in the A-band ; this leads to a "hole" in the 279 nm emission spectrum.

The study of the emission spectra of KCl:Tl and KBr:Tl made by Edgerton and Teegarden(15), Williams and Johnson(110), Lushchik and Co-workers(111) revealed that the emission spectra of these compounds are not as complex as that found for KI:Tl. However, high energy emission bands, not previously observed, have been found in these two additional cases. In KCl:Tl, besides the well-known band at 305 nm, a band centred near the position of the A - absorption band has been discovered at 80°K and 12°K. This emission band is strongly reabsorbed in the A - band, so that its position is hard to determine accurately.

Only these two bands are well - defined . However, the evidence, that the band which appears at 305 nm is actually composed of two strongly overlapped bands, has been given by several workers including Edgerton(10), Edgerton and Teegarden(109), Patterson and Klick(22), Patterson(23).

The polarization properties of the absorption and emission bands were investigated and it was found that these experiments agree in certain respects with a forgoing model. According to Kilck and Compton(112), when KCl:Tl is irradiated at 4°K with linearly polarized light in the A - band region, the emitted light is also linearly polarized, preferentially along (100) axis.. The polarisation is not present at 77°K. Since then, these experiments have been extended by others. Edgerton(113) found that in the case of KI:Tl at low temperature, A - band excitation led to polarized emission at 336 nm; B and C band excitation yielded polarization in the 289 nm and 279 nm bands respectively, and no polarization in the 305 nm, 336 nm, or 413 nm bands..

In the theoretical discussions (Knox(14) , Williams and Johnson(110)), an emission band at 475 nm in KCl:Tl, which has been reported in earlier work, has played a considerable role. The band appears not to be due to a simple substitutional thallous ion. Its intensity relative to the bands just described depends upon the concentration of the impurity and the state of perfection of the crystal (Ivanova el al.[(14)]). It does not appear in single crystals with low concentrations of thallium. It is known that, at 80°K, excitation in the A-band produces only the 305 nm band, while excitation in the C-band produces both emission bands. Detailed investigations of the excitation spectrum of KCl:Tl have not been made at the lower temperatures. In the emission spectrum of KBr:Tl, two poorly resolved bands appear at 300°K. These are more completely resolved at 80°K and a new band appears at 260 nm centred on the A-absorption band, so that it is reabsorbed at the centre. At 12°K the 362 nm band is quenched relative to the shorter wavelength emission. It is known that at 300°K excitation in the A, B or C bands produces the same emission. At 80°K excitation in the A-band produces the two bands at 362 nm and 310 nm, while excitation in the B and C bands produces all three emission bands. No detailed measurements of the excitation spectrum appear to have been made at temperatures below about 80°K.

The striking feature in the emission spectra of all three systems at 12°K (or extrapolated to 0°K) 100°K is that they are very much similar to each other. There is one emission band at longer wavelength than any of the absorption bands and emission which strongly overlaps and is absorbed by the A-band. It has been suggested by Edgerton and Teegarden(15) that the emission spectra of KBr:Tl and KCl:Tl at different temperatures can be explained in the same terms used in the forgoing for KI:Tl if it is assumed that as the host anion gets lighter, the ^3P_o and $^3P_1$ levels approach each other, while at the same time the $^1P_1$ and $^3P_2$ levels approach each other. In this interpretation the 362 nm band of KBr:Tl is attributed to the $^3P_1$ level. The band (or bands) which superimposed on the A-absorption band is attributed to $^1P_1$ or $^3P_2$ or both. In KCl:Tl the same interpretation is given to the high-energy emission band. It is suggested by these workers that the lower lying component of the 305 nm band of KCl:Tl is due to ^3P_o and that the higher energy component originates from $^3P_1$.

Vaidanich and Teegarden(2) studied the emission spectrum of NaI:Tl at 12°K which also indicated that the A-band is not single at these temperatures. Excitation on the long-wavelength side of the A-band in the heavily doped NaI crystals results in emission at 435 nm. This emission band is analogous to the 430 nm band of KI:Tl and hence it has been ascribed to the $^3P_0$ state by Edgerton and Teegarden(109). At high temperature this hand appears during irradiation in the A-band but at 12°K it is quenched in lightly doped crystals. Irradiation in the peak of the A-band in both, NaI and KI, at 12°K produces a shorter wavelength emission that is ascribed to the $^3P_1$ state the discussion above.

e) THALLOUS ION PAIR (DIMER) LUMINESCENCE :

Many investigators have studied both experimentally and theoretically optical properties of several alkali halides crystals containing thallium in low concentrations(1). However, in alkali halide crystal containing rather high concentration of thallium, one may observe new absorption and emission bands which do not appear in lightly doped (115). Yuster and Delbecq(95) studied the absorption spectra of KI crystals heavily doped with thallium. They found several new absorption bands whose maximum absorption coefficients vary as the square of the thallium concentration, and assumed that these bands arise when two thallous ions occupy the nearest neighbour alkali ion sites. Similar absorption bands have been observed in NaI crystals containing thallium in high concentrations. T. Tsuboi(116) has studied absorption, emission and excitation spectra of KI:Tl, KBr:Tl, KCl:Tl and KCl:In crystals from 15°K to 300°K. Five absorption bands, which were ascribed to the Tl^+ dimer centre, were observed in addition to the Tl^+ monomer absorption bands in highly doped crystal (> 0.01 mole %). It is interesting to note that, although the dimer absorption bands fall rather close to the single ion, or monomer bands, the emission bands are quite distinct from one another. No paired thallous ion centre in other alkali halide crystals have been reported yet.

3.5 RECENT INFORMATION :

Recently Tsuboi(117) has investigated absorption, emission and excitation spectra of KBr crystals with high Tl^+ concentration at 15°K and 77°K. The absorption bands at 262, 229 and 217 nm were attributed to Tl^+-trimer centre composed of three Tl^+ ions and have been identified which once related to the A, B and C bands of Tl^+ monomer centre respectively. Tsuboi(118) also studied absorption spectra of KI crystals with high Tl concentration after X-ray exposure at 77°K or 120°K. He suggested that the new band observed at 1800 nm can be ascribed to Tl_2^+ centres which are formed when $(Tl^+)_2$ centres capture electrons created in the crystal by the X-ray exposure or released from Tl° centres.

M. Ishiguro(119) <u>et al</u>. have measured the absorption spectra of Tl_2^+ in KCl crystals from 77° to 300°K . They suggested that the Tl_2^+ gave rise to five absorption bands. Optical excitation in the 460 nm band destroys the Tl_2^+ and Tl^{++} bands and produces Tl° bands. Thermal excitation of a crystal containing only Tl_2^+ and Tl^{++} results in the simultaneous decay of Tl_2^+

and Tl^{++}. Electrons released from Tl_2^+ by optical or thermal excitation are trapped at Tl^+ and Tl^{++}. According to the authors, a Tl_2^{+++} is formed when a $(Tl^+)_2$ traps a positive hole of a nearby Cl_2^-, whereas it is destroyed when a Tl_2^{+++} traps an electron released from a Tl_2^+ by optical excitation in the 460 nm band.

Experimental evidence on the triplet structure of the A-absorption band in KBr:Tl has been reported(120). Thermostimulated absorption measurements for KBr:Tl taken between 282 nm and 206 nm and at 88°K and 293°K helped in deducing the band multiplicity and the band positions(121). The impurity behaviour was shown to be strongly affected by the electron lattice interaction.