CHAPTER I

INTRODUCTION

Luminescence and the related electrical properties of the crystals are some of the striking effects that are brought about by the introduction of impurities. During the last two decades, considerable amount of work has been carried out in the field of luminescence of solids which has helped in obtaining deeper understanding of the various branches of solid state physics. Methods and concepts of the luminescence processes in solid phosphor therefore occupy a key position in the study of solid state physics. Since the results obtained with crystals of simple structure and known properties in the pure state would be more amenable to interpretation, alkali halides have been widely used as host crystals for fundamental researches on phosphors. Alkali halides are still the predominant subjects for study in the present-day luminescence research. Their lattices are cubic and many of their properties are profoundly affected by strong coulomb interaction which result from the highly ionic nature of these solids. Their large binding energies ($\sim$200 KCal/mole) result in high melting point ($\sim$1000°K) which offers a vast range of temperatures over which phenomena may be studied. The large electronic band gaps ($\sim$8 ev) of these solids result in wide range of optical transparency and thus a very broad spectral region is available for the study of the effects of impurities, vacancies and other crystalline defects.

Alkali halides do not luminesce strongly in the pure state, until the temperature is lowered below the boiling point of liquid nitrogen (77°K), although a weak luminescence has been studied by Timusk[1] at 300°K. Measurements of the emission spectra of these compounds excited with ultraviolet light at 12°K have also been undertaken[2]. Attempts have been made to investigate the nature of the centre responsible for the intrinsic luminescence of the alkali halides. First of all, Weeks and Teegarden[3] showed that an emission identical with intrinsic luminescence can be stimulated by irradiation in the F or F' bands formed by exposure to ultraviolet light at 93°K. 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 recombine.

Kabler[4] and Murray and Keller[5] studied the luminescence of several of the alkali halides stimulated by X-irradiation at low temperature. Emission spectra obtained in this way were similar to but not identical with those obtained by excitation with ultraviolet light. These workers demonstrated that the intrinsic luminescence can also be stimulated by irradiation in the F and F' bands formed by previous exposure to X-rays at low temperature, in analogy with the experiment of Weeks and Teegarden[3].

A small amount of thallium introduced in an alkali halide produces a luminescent material of considerable fundamental interest. Much experimental and theoretical work has been reported on the optical absorption and luminescence of alkali halide crystals containing thallous ion impurity[6-14]. Such a phosphor exhibits two strong absorption bands on the long wavelength side of the fundamental absorption edge. To explain its experimental features, Seitz[7] proposed a model in which activator ions enter the lattice substitutionally at cation sites. Thus, according to Seitz, Tl^+ ions replace alkali ions in alkali halide lattice. The Seitz model is better suited to detailed theoretical study and has been the basis for the only quantitative computations yet attempted in the luminescent system[8]. Subsequent experimental results however revealed that apparent simplicity of the thallium-doped alkali halide system was an illusion and that a more complex problem must be dealt with before a complete solution is obtained. Typical are the facts that both A and C bands (of Seitz' terminology) are quite asymmetric at room temperature but sharpen into essentially symmetric bands at low temperatures[15] and that the excitation of the two emission bands occurs in two separate portions of the A band rather than a single one[16-18]. Excitation and high temperature absorption study of KCl:Tl led Patterson[19] to conclude that in KCl:Tl there are at least three bands in A region and two such in B and C regions. To account for these and some other results, some authors[17-19] suggested that there are at least two types of luminescent centres with different excitation and emission spectra. It was found that, in alkali halides that were not lightly doped with thallium, absorption of some of the bands increased faster than linearly with thallium concentration and these bands were therefore suggested to be associated with pairs of nearby thallium ions or their larger aggregates[19]. Thus, the two kinds of luminescent centres suggested to explain the luminescence of KCl:Tl phosphor are: (i) Tl^+ ion replacing K^+ ion at the lattice sites and (ii) Tl^+ ions in pairs or higher aggregates occupying nearest neighbour K^+ ion positions in the lattice.

Thallium activated alkali halide systems that have been studied in more detail in regard to their absorption and emission properties are KCl:Tl; KBr:Tl and KI:Tl. Although there is no particular indication from earlier work that Tl^+ ion will behave substantially differently in other host crystals, in fact other systems such as NaCl:Tl etc. have not been studied in detail. The choice of NaCl:Tl system in the present work arose out of this consideration. In size, Tl^+ ion is comparable with K^+ ion (Tl^+ ion radius = 1.44 Å; K^+ ion radius = 1.33 Å) whereas it is large relative to Na^+ ion (Na^+ ion radius = 0.95 Å). It is therefore to be expected that the behaviour of KCl:Tl and NaCl:Tl system may not be similar in all respects. The results obtained in the present work bear this out. It is found that especially at higher thallium concentration the behaviour of the two systems is markedly different. For instance, predominance of visible emission bands observed in KCl:Tl phosphors at high thallium concentrations is conspicuously absent in NaCl:Tl system.

The present experiments involved the study of the excitation and the emission spectra of the phosphors at room temperature. The phosphors were in the form of micro-crystalline powder varying in thallium concentration in the range $\sim 10^{-4}$ to 10^{-1} molar fraction. Specimens were studied in as-received condition after their preparation by crystallization from aqueous solution and also after thermal treatments followed by deformation or in the undeformed state. One of the noteworthy features of the present experiments is that excitation and emission measurements have been carried out in a way which permits the correlation of wavelengths so that one can tell which emission band is favoured by a given excitation. Measurements on the excitation and emission spectra of undoped TlCl powder, aqueous TlCl-solution and TlCl in aqueous NaCl-solution have also been made. All these measurements were carried out at room temperature. The excitation bands observed in the current investigation, together with the emission bands excited by them, are discussed in certain groups to suit the convenience. In principle, the three emission band groups can be distinguished on the basis of the spectral region in which they appear. The three groups are emission bands in the (i) Ultraviolet, (ii) Near-ultraviolet, and (iii) Visible region. The principal results are : (i) Solid NaCl:Tl phosphor, TlCl powder and aqueous TlCl-solution have common luminescence characteristics in regard to their emission in the near-ultraviolet region. (ii) Parallelism exists between the luminescence spectra of aqueous NaCl-solution containing TlCl and heavily-doped solid NaCl:Tl phosphor. It is concluded that besides isolated substitutional Tl^+ ions the other types of centres responsible for the luminescence of NaCl:Tl crystal phosphor could be (a) TlCl molecules and (b) complex ion centres of the type $(TlCl_n)^-$.