CHAPTER - I

INTRODUCTION

Luminescence is one of the oldest and the most established analytical techniques. Although luminescence, as such, was known for a long time past, it was not until the middle of the nineteenth century that it was subjected to systematic study. Historically, the first law of luminescence was formulated by Stokes in 1852. It is known as Stoke's rule and states that the wavelength of luminescence excited by radiation is greater than the wavelength of the exciting radiation. At about the same time Becquerel laid the foundations for the experimental investigation of the emission spectrum, the efficiency of excitation and the duration of luminescence afterglow (phosphorescence). In 1889 Wiedemann introduced the term 'luminescence' and gave the first, although not entirely accurate, definition of this phenomenon as the excess emission over and above the thermal emission background.

Luminescence of solids continues to be rewarding field for scientific study and practical applications. It gives us a new outlook on the behaviour of energy and matter, in a realm which has recently become a cornucopia of useful and fundamental information - solid state physics. Solid state physics is mainly concerned with physical properties of solids, particularly the special properties exhibited by its atoms and molecules, because of their association in the solid phase. Methods and concepts of the luminescence processes in solid phosphor occupy a key position in the study of solid state physics. The practical use of luminescence phenomena, now a days, is very wide. It is commercially used in fluorescent lighting, cathods ray tubes for radar, and television, advertising paints, scintillation counters, solid state lasers and image intensifiers.

For the fundamental researches on phosphors alkali halides have been widely used as host crystals, because they are the best known of the halide structures. Since they are easily obtained in the form of large single crystals, the data on them are perhaps more reliable. They crystallize in cubic structure and due to their highly ionic nature, many of their properties are profoundly affected by strong coloumb interaction. Their large binding energies ($\sim$ 200 K Cal/mole) result in high melting point ($\sim$ 1000°K)which offers a vast range of temperatures over which phenomena may be studied.

Of outstanding importance for the study of luminescence phenomena is the extraordinary wide range of optical transparency shown by the alkali halides. This is because of large electronic band gaps (~ 8 ev) of these solids.

It was found that in the pure state alkali halides do not luminesce strongly, until the temperature is lowered below the boiling point of liquid nitrogen (77°K). A weak luminescence has been studied by Timusk(4) at 300°K. Attempts have been made to investigate the nature of the centre responsible for the intrinsic luminescence. Single crystals of the alkali halides luminesce strongly at low temperature when irradiated with ultraviolet light absorbed in exciton and interband transitions(5,6). Both an intrinsic emission and the characteristic luminescence of certain impurities can be stimulated by this means. The intrinsic emission, so called because it can apparently occur in a perfect crystal, is due to the recombination of an electron with a V_k - centre or self-trapped hole. Emission spectra of single crystals of KI and RbI were studied at 10°K and results obtained show two prominent emission bands. On the basis of an extensive study of crystals from different sources it has been concluded that these emission bands in KI and RbI are an intrinsic effect(7). They do not depend upon the source or history of the samples, and are not excited by photon energies outside the intrinsic absorption region of the crystals. It was shown by Weeks(8), Teegarden(9) and Weeks and Edgerton(10) that the intrinsic emission bands of KI and RbI are due to the recombination of an electron with a trapped hole.

The greatest interest has been centred in the alkali halide phosphors, activated by heavy metal inclusions and having good luminescence efficiencies. Experimental and theoretical work on the optical absorption and luminescence of alkali halide crystals containing thallium ion impurity have been pursued much vigorously(3,11-18). When a small amount of thallium is introduced into an alkali halide, it exhibits two strong absorption bands on the long wavelength side of the fundamental absorption edge. Seitz(3) explained its experimental features by suggesting a model according to which activator ions enter the lattice substitutionally at cation sites. The Seitz model is better suited to detailed theoretical study and has been the basis for the only quantitative computations yet attempted in the luminescence system(12). Subsequent experimental results however showed that apparent simplicity of the thallium doped alkali halide system was an illusion and that a more complex model 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 assymetric at room temperature but sharpen into essentially symmetric bands at low temperatures(19), and that the excitation of the two emission bands occurs in two separate portions of the A-band rather than a single one(20-22). Excitation and high temperature absorption study of KCl:Tl led Patterson(23) 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(21-23) suggested that there are at least two types of luminescence 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

substitutional thallous ions or their larger aggregates(23). Thus two kinds of luminescence centres suggested to explain the luminescence of KCl:Tl phosphors were :
(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.

The luminescent feature of NaBr:Tl phosphor might apparently be thought as similar to that of KCl:Tl and other extensively studied thallium doped alkali halide phosphors. Further, NaBr being highly hygroscopic, study of NaBr:Tl phosphor has not attracted much attention so far. However, the usefulness of the phosphors like NaI:Tl, NaBr:Tl as high energy particle detectors has necessiated detailed investigation of their luminescent properties. The luminescent behaviour of the thallium doped alkali halides has been in general assumed to be more or less similar, because most of the properties of the heavy metal impurities in the alkali halides are dependent only upon the interaction of the impurity with six nearest neighbour halogen ions. Present investigations were undertaken to test the validity of the above assumption and the results obtained indicate that such an assumption is in doubt. In size, Tl^+ ion is comparable with K^+ ion (Tl^+ ion radius = 1.44 A° ; K^+ ion radius = 1.33 A°) whereas it is large relative to Na^+ ion (Na^+ ion radius = 0.95 A°). Thus from volume considerations Tl^+ ions are misfits into NaBr lattice. It is therefore to be expected that the behaviour of thallium doped potassium halides may not be similar in all respects to thallium doped sodium halides.

In the present investigations the excitation and emission spectra of the lightly as well as the heavily doped phosphor have been measured after UV - - irradiation at room temperature. The specimens used in the work were microcrystalline in nature prepared by crystallization from aqueous solutions. The doped crystals utilized contained the thallium concentration varying from 10^{-4} to 10^{-1} m.f. The phosphors were studied in as-received condition and also after thermal treatment and thermal treatment followed by deformation. 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. In a related study, the excitation and emission spectra of TlBr - powder, aqueous TlBr -

- solution and NaBr - solution were also examined. The data obtained leads one to conclude that besides substitutional Tl^+ ion and Tl^+ ion pair centres reported earlier by other workers, other types of centres are also possible in NaBr:Tl system. These additional centres are : (i) TlBr - molecule (ii) Charged complex ions of the type $(TlBr_n)^-$ and (iii) Na^+ ion in TlBr lattice.