CHAPTER-I

GENERAL INTRODUCTION

1.1. INTRODUCTION :

The imperfection controlled properties of real crystals are better understood through their mechanisms of colouration, optical absorption and luminescent properties which constitute some of the major aspects of the subject matter of Defect Solid State Physics. The lattice defects which are invariably present in real crystals play the central role in unravelling the realities of nature and may be broadly classified into two categories viz.

(i) Structural defects present inherently in the crystal and are induced by foreign atoms/ions, vacant lattice sites and interstitial atoms/ions. A variety of luminescence and allied phenomenona have been observed (1,2) due to the presence of localised energy levels in the band gap (fig. 1.1) induced by the incorporation of even very small amounts of the foreign atoms of the same or different valency state in the lattice.

(ii) Radiation induced defects produced by exposing the crystals to ionising radiations like X-rays cause charge separation and subsequently produce excitons or electron and holes. The free electrons and holes thus produced get trapped individually leading to the formation of a large variety of colour centres which take part in various electronic processes in the lattice. A schematic diagram of the energy levels of these colour centres along with their involved electronic processes is presented in fig. 1.2.

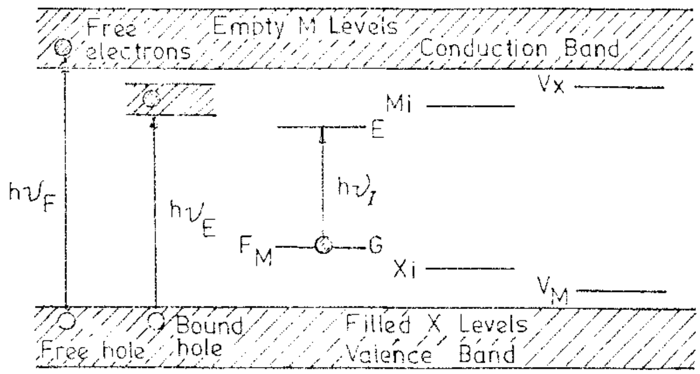

FIG.1.1: POSSIBLE ENERGY LEVELS OF THE PARENT LATTICE IONS M^+ & X^- FOREIGN CATIONS F_M, CATION AND ANION INTERSTITIALS Mi & Xi AND CATION AND ANION VACANCIES V_M & V_X IN AN IONIC CRYSTAL MX. OPTICAL TRANSITIONS CORRESPONDING TO FUNDAMENTAL ABSORPTION ($h\nu_F$) EXCITON ABSORPTION ($h\nu_E$) AND IMPURITY ABSORPTION ($h\nu_I$) PRIOR X IRRADIATION ARE SHOWN.

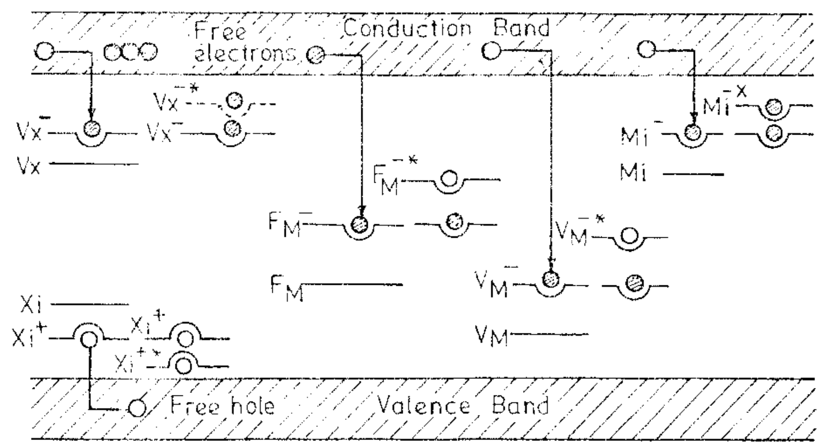

FIG.1.2: X IRRADIATION EFFECT ON THE CRYSTAL OF FIG 1.1. THE FORMATION OF ELECTRON AND HOLE TRAPS AND OPTICAL ABSORPTION DUE TO THESE TRAPPED ELECTRONS AND HOLES ARE AS SHOWN.

Amongst a large variety of ionising radiations, X-rays are preferred in the present work because of the simple reason that X-ray excitation is comparatively homogeneous and affects the whole bulk of the crystal. Prolonged irradiation with X-rays creates a large number of radiation induced defects in addition to the structural defects. The temperature of X-irradiation as in the cases of other ionising radiations, plays a vital role in the defect formation mechanism and as such colour centres formed at one temperature may not be formed at other temperature and some times vice-versa. One disadvantage, however, is that with prolonged X-irradiation, a permanent damage leading to chemical changes in the crystal may take place limiting the repeated use of the same sample, which is proved to be essential for the reproducibility of the results in many cases.

Because of the diversified technological importance the study of point defects has found their rightful place in solid state research in the current age. Alkalihalides have been proved to be ideal solids offering ample scope for experimental as well as theoretical investigations of such point defects. This is largely because of the strong coulomb interactions resulting in large binding energies ($\sim$ 200 KCal/ mole) and consequently high melting points ($\sim$ 700°C) which provide a wide range of temperatures in which the associated physical phenomena can be effectively studied. Furthermore, large binding energies are related to large electronic band gaps ($\sim$8eV) providing a broad transparent spectral region in which the effects of vacancies interstitials impurities and other defects can be studied. The choice of KCl crystal, in the present work, among all other alkali-halides lies in the fact that not only because of its simple structure and availability in the form of single crystals, it can be grown in the highest possible degree of chemical purity and as such the effect of a very small amount of impurity can be efficiently detected and studied. The KBr crystals, though not found in a very high degree of chemical purity, have proved to ba a very suitable host for the monovalent cation impurities like Li^+ (3-5) and Na^+ (6,7) ions as regards defect properties are concerned. Hence the present work embodies the point defect studies in pure and Li^+-doped KCl and KBr single crystals right from liquid nitrogen temperature (LNT) to 350°C.

1.2. THE SCOPE AND CONTENT OF THE PRESENT INVESTIGATION :

The principal object of the present work is to study the mechanism of formation, thermal and temporal stability, the behaviour manisfested electronic processes of point imperfections, - both structural and radiation induced, - stable and transient - in pure and monovalent cationic doped alkalihalide crystals over a wide temperature range (LNT to 350°C). The physical property changes like optical absorption and luminescent behaviour both during and after irradiation along with the process of annihilation of the defect centres produced by irradiation are the efficient agents from which the knowledge regarding the