CHAPTER-I

GENERAL INTRODUCTION

1.1. INTRODUCTION :

Among the various studies, such as optical absorption, thermally stimulated luminescence ESR, EPR, ENDOR, dielectric relaxation, conductivity, Stark and Faraday effect, etc., that have been pressed into service to study the imperfection controlled properties of solids, Opto-electronic property studies gained importance not only for understanding the basic defect solid state but also due to the applicational potentiality of such materials prepared with controlled amounts of defects and imperfections. Of the various opto-electronic property studies, thermally stimulated luminescence is a relatively recent candidate for understanding the luminescence oriented defect solid state. The existence of the lattice defects which may be either structural defects arising out of the presence of inherent impurities/ deliberately doped foreign atoms / ions or the radiation induced stabilised defects, leads to the presence of localised energy levels in the energy band gap of these materials. Since the presence of lattice imperfections alters / medifies the opto-electronic properties of the solids to a great extent, such lattice defects can be characterised by studies based on luminescence and allied optoelectronic phenomena [1,2,3]7. Further, opto-electronic properties are strongly influenced by the method of defect production, the mechanism of defect formation and temperature of defect production $Z_{4}7.$

Radiation induced defect centers are produced when the ionic solids are exposed to ionising radiation like X-rays. The free

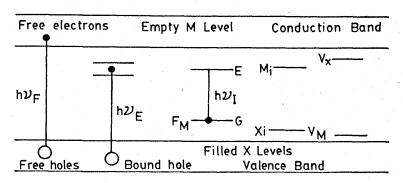


Fig 1.1: POSSIBLE ENERGY LEVELS OF THE PARENT LATTICE IONS M* AND X FOREIGN CATIONS FM CATION AND ANION INTERESTIALS M; & X; AND CATION & ANION VACANCIES V_M AND V_X IN AN IONIC CRYSTAL MX OPTICAL TRANSITIONS CORRESPONDING TO FUNDAMENTAL ABSORPTION (h ν_F), EXCITATION ABSORPTION (h ν_F), IMPURITY ABSORPTION (h ν_I) PRIOR TO X-IRRADIATION ARE SHOWN.

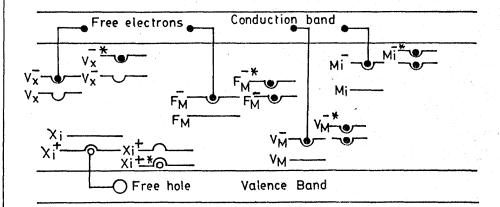


Fig 1.2: THE IRRADIATION EFFECT ON THE CRYSTAL OF Fig 1.1. THE FORMATION OF ELECTRON AND HOLE TRAPS AND EXCITED STATES DUE TO THESE TRAPPED ELECTRONS AND HOLES ARE SHOWN.

electrons and holes produced by irradiation are trapped by the corresponding electron traps or hole traps, finally resulting in the variety of electron and hole centers. The electron and hole centers so formed, interacting among themselves or with the excitons, take part in the recombination processes ultimately giving rise to the luminescence emission. The schematic diagram of the energy levels of these defect centers along with their electronic processes is shown in Figs. 1.1 and 1.2.

Amongst a variety of ionising radiation, X-rays are preferred to because the X-ray excitation is homogeneous and effective throughout the bulk of the crystal. Irradiation with, X-rays creates a variety of radiation induced stabilised defects in addition to the structural defects. The thermal stability of these radiation induced defects depends on the temperature or irradiation and as such the defects produced and stabilised at one particular temperature may not be stabilised at another temperature and vice versa. One disadvantage is that prolonged irradiation causes a permanent damage leading to chemical changes in the crystal. This prevents the usage of the same crystal repeatedly which is proved to be essential for the reproducibility of the results in many cases.

· Studies on defect centers in ionic solids, centre around alkali halides since they offer the proving ground for the models formulated and theories profounded. i.e. they are the test solids for experimental and theoretical investigations. In the present

investigation, the systems undoped, Na+ and Ca++ doped KCl single crystals are chosen for the study. The reasons for the selection of such materials are that the alkali halides are the typical materials having a band gap of 8 eV, providing a wide transparent region, in which the effect of impurities, vacancies and other defects can be profitably studied. Moreover, because of the strong coulomb interactions, resulting in large binding energies (200 K Cal/mole) and consequently high melting point (pprox 700°C). these materials provide a wide range of temperatures over which a variety of physical phenomena can be studied. The choice of KCl crystals, among the alkali halides, lies in the fact that it can be grown in highest possible degree of chemical purity and as such the presence of even trace amounts of impurity can be efficiently defected and studied. Further, KCl crystals are found to be suitable hosts for the monovalent cation impurities like Lit, and Na^{+} $\begin{bmatrix} 5.6 \end{bmatrix}$ as well as a variety of divalent impurities $\begin{bmatrix} 7.7 \end{bmatrix}$. It is observed that Na in KCl produces an interesting and appreciable colouration at RT as well as LNT, because the presence of Na impurity modifies / stabilises the intrinsic defects like $\mathbf{V}_{\mathbf{k}}$ and \mathbf{F} centers giving rise to various types of modified defects like V_{kA} , V_{F} , H_{A} , H_{AA} , H_{AA} , F_{A} , F_{B} , F_C etc. \angle 8, 9, 10 $\underline{\ 7}$. Moreover, doping of KCl with alkaline earth impurity Ca++ , has been equally rewarding in the sense that, because of their low ionisation potential, they give rise to new defect centers like \mathbf{Z}_1 , \mathbf{Z}_2 , \mathbf{Z}_3 , \mathbf{Z}_4 etc. centers $\boxed{11\cite{1}}$. Further, incorporation of Ca++ impurity in KCl lattice produce an