CHAPTER -1

GENERAL INTRODUCTION, SCOPE, CONTENTS AND AIM OF THE PRESENT WORK

1.1 INTRODUCTION

The physical properties of solids are influenced considerably by the defects present in them. Real solids contain a number of lattice defects like impurities, vacancies, interstitials, dislocations etc.; the nature and concentration of such defects may vary from sample to sample depending on its thermal and mechanical history and also on the impurity content. The investigation of the changes in the physical properties with controlled variation of lattice defects is of considerable importance from theoretical as well as experimental point of view. Such a study paved the way for applications of some of the materials in technology. Apart from these defects, separation of electric charges leading to local variation in charge density (from that available in normal crystals) may also occur in some cases; such defects can be easily induced by irradiation with ionising radiations like X-rays and \( \vec{\gamma} \)-rays. X-ray irradiation generally gives rise to internal photoelectrons, which may get trapped at the special lattice sites having localised potential barriers, and does not, in most cases, cause any displacement of the constituent atoms or ions from their original lattice positions. The imperfections, produced by X-ray irradiation in a material, are, therefore, considered simple in structure
and hence the physical properties of solids on X-ray irradiation has become the subject matter of many investigations\textsuperscript{1-3}.

All crystals are commonly classified into seven systems depending on their geometry: triclinic, monoclinic, orthorhombic, tetragonal, trigonal, hexagonal and cubic. These systems can again be subdivided into 32 point groups according to their symmetry with respect to a point and 11 of them possess a centre of symmetry (centrosymmetric). Of the remaining 21 non-centric crystal classes, all except one (432) exhibit electrical polarity when subjected to stress and also its converse, the production of strain by application of an electric field. The effect is linear and this phenomenon is called piezoelectricity. Ten of 20 piezoelectric point groups are characterized by the fact that they have a unique polar axis. Crystals belonging to these classes are called polar because they possess a spontaneous polarization($P_s$) or electric moment per unit volume. The magnitude of $P_s$ changes with temperature and these crystals are therefore called pyroelectrics for which the direction of $P_s$ cannot be reversed by applying an electric field. A ferroelectric crystal is a pyroelectric, in which the polarization can be reversed or reoriented by applying a sufficiently large electric field in the appropriate direction for a relatively short time. The electric field can reverse the polarization by making a small relative displacement of the atoms in the crystal.
The physical properties of ferroelectrics have been extensively studied and reported\textsuperscript{4-11}; such studies gave considerable understanding of the phenomenon of ferroelectricity. The application of these materials in industry, for example, in the manufacture of transducers, high value capacitors, dielectric amplifiers, memory devices, electro-optical and optical parametric devices, is well known\textsuperscript{12,13}.

According to the crystal-chemical classification, the ferroelectric compounds are divided into two groups. The first group comprises of hydrogen-bonded crystals, such as rochelle salt, KDP, TGS etc. The second group includes oxides, such as BaTiO\textsubscript{3}, KNbO\textsubscript{3}, Cd\textsubscript{2}Nb\textsubscript{2}O\textsubscript{7} etc.

The ferroelectric nature of a material can be established by studying its dielectric properties and hysteresis loop as a function of temperature. Dielectric constant exhibits enormous increase around curie temperature ($T_{c}$) and decreases immediately beyond $T_{c}$ with increasing temperature following Curie-Weiss law. Apart from these studies, temperature dependence of spontaneous deformation, linear expansion, piezoelectric constant, elastic compliance and specific heat measurements can also be used as tools to investigate the ferroelectric properties of materials.

The properties of ferroelectrics are found to be affected considerably by the lattice defects present in them, viz.,
the nature and concentration of impurity, lattice vacancies etc.\textsuperscript{14}. For example, the presence of strontium impurity is found not only to change the dielectric properties of BaTiO\textsubscript{3}, but also to lower its curie temperature\textsuperscript{13}. Concept of the existence of lattice vacancies and their accumulation on the surface of a BaTiO\textsubscript{3} crystal forming space charge layers have been found necessary for explaining a number of experimental results, for example, asymmetric pyroelectric effect, asymmetric hysteresis loops, thickness dependence of coercive field etc.\textsuperscript{15,16}. Detailed studies on BaTiO\textsubscript{3} or TGS showed that even very small doses of X-ray irradiation can give large changes in the dielectric and allied properties of the ferroelectric materials, for example, formation of double hysteresis loops, increased coercive field, and a decrease in dielectric constant (particularly at low frequencies\textsuperscript{17,18}) and direct evidence of domain clamping supported by optical studies. With increasing dosage the dielectric constant peak and polarization curve broaden and move to lower temperature\textsuperscript{19,20}. Effect of X-ray irradiation\textsuperscript{21} and D.C. biasing on BaTiO\textsubscript{3} and its composite crystals\textsuperscript{22} yielded valuable information regarding fundamental processes taking place in them.

There are certain materials such as SrTiO\textsubscript{3} which exist in non-polar condition with a close similarity of polar one, which has no hysteresis loop observable below T\textsubscript{C} but it has a high dielectric anomaly at the transition temperature T\textsubscript{C}. An applied field(E) decreases T\textsubscript{C}, by contrast with the increase
of $T_c$ in ferroelectrics. At sufficiently high field strengths, these crystals become ferroelectric, although not necessarily along the same axis. An important example is strontium titanate. It possesses non-ferroelectric structural phase transitions involving oxygen-cage tilting, at about 105K. At high temperature the dielectric response follows a Curie-Weiss law suggesting a ferroelectric phase transition at about 35-40K. At lower temperatures, however, the dielectric constant never peaks at atmospheric pressure but continues to rise down to helium temperatures. It shows electric hysteresis loops (indicating a ferroelectric structure) which is found below another (lower) transition at 55K, but there is uncertainty about SrTiO$_3$ structure and recently (Saifi and Cross) reported double loops. Subsequently it has been established that pure SrTiO$_3$ single crystals are not ferroelectric.$^{23}$

Another set of solids the physical properties of which are very much controlled by the lattice defects in them and hence have been extensively studied are alkali halide crystals.$^{24,25}$ These contain a number of lattice imperfections like vacancies, interstitials, dislocations, impurities etc. In fact, assumption of the existence of such defects has become necessary for explaining many important experimental findings in these solids.

The concepts in defect solid-state are developed from an intensive study of the colouration phenomena in the alkali
halides which are in many ways considered ideal solids for experimental and theoretical investigations because they have simple cubic structures, are obtainable in a reasonable degree of chemical purity and are amenable for growth in large single crystals. However, many experimentally observed properties of these materials could not be explained without assuming that the real crystals fall short of the ideal, highly ordered structure. They contain structural imperfections mentioned earlier; vacant lattice sites and/or interstitial ions along with a small number of dislocations present in real crystals are generally formed during the growth process itself. Vacancies and/or interstitial ions can also be produced by chemical impurities which are intentionally added to the host material or are intrinsically present in it. For example, foreign atoms of the same or different valency existing in the crystal even in a few parts per million concentration, give evidence of their presence by introducing new electronic levels and new absorption bands (Fig.1.1). Such disturbances in the electronic configuration of a material may bring about changes in its physical properties like dielectric, magnetic, mechanical etc.

X-ray irradiation of an alkali halide crystal produces new absorption bands in the normally transparent spectral region; these bands are due to colour centres which are electrons and holes trapped at special lattice sites. In pure crystals, generally the colouration is characteristic not only of the process of colouration but is also strongly influenced by the