1. INTRODUCTION

This chapter introduces the actual work done by the author along with some background information related to the present topic of research. It also gives a review (though not comprehensive) of various studies made on alkali halide mixed crystals in the near past.

1.1. Crystals and Their Importance

The word 'crystal' stems from the Greek word 'Krystallos' meaning 'clear ice'. It was applied to the clear crystals of quartz found in Swiss Alps. Such crystals actually reflect a highly symmetric and periodic internal arrangement of atoms.

Matter exists in three physical states which are solid, liquid and gas. In the case of solids the atoms, ions or molecules are held together by relatively strong chemical forces. But in the case of liquids and gases they are loosely bounded. Matter in the solid state can be classified into three categories. They are: crystalline, amorphous and quasi-crystalline states. The crystals differ from non-crystals in the way that the atoms are stacked in a regular manner in the crystals.

Crystals can be considered as regular polyhedral form bounded by smooth surfaces, which is assumed by a chemical
compound under the action of its interatomic forces, when passing from the state of a liquid or gas to that of a solid under suitable conditions. In the case of crystalline substance the melting point is very sharp and they are compressible and rigid.

In crystals the atomic array is periodic, i.e., the atoms are arranged in a regular pattern. In non-crystals the same atomic groups are arranged more randomly. This is true for all non-crystalline materials. Solids which contain atoms in ordered arrays, but the pattern they assume are subtle and do not recur at regular intervals are said to be quasi crystals.

Normally in single crystals the periodicity extends throughout the material. In an ideal single crystal every atom is surrounded by a precisely uniform spatial arrangement of other atoms and it is free from inner boundaries. But, if a crystal is having inner boundaries along with external boundary, it is called poly crystalline.

Real crystals often exhibit a variety of imperfections in the regularity of arrays, viz. dislocation, twinning and other kinds of defects. But the specimen under study should be perfect and three dimensional. So, for scientific research purposes, the researchers will grow crystals in the laboratory to their own taste.

Man had admired crystals for long as he had appreciated beauty. Crystallization of salt is mentioned in a Chinese reprint of 2700 BC. Crystals have fascinated men and
women for many thousands of years. Naturally occurring hard gem stone crystals were priced along with gold in antiquity.

Crystals are the pillars of modern technology. Crystals play a vital role in electronic industry, photovoltaic solar cells, fibre optic communications, detecting instruments, scintillators and in space technology. Integrated micro-electronics and opto electronics necessitate improved crystal growth technology for large diameter silicon, GaAs and InP in combination with optimized defect and property control on submicron scale. Laser fusion energy depends on high power laser crystals and oxide crystals.

Crystal growth is a vital and fundamental part of material science and engineering, since crystals of suitable size and perfection are required for fundamental data acquisition and for practical devices such as detectors, integrated circuits and for other millions and millions of applications. The ever increasing application of semiconductor based electronics creates an enormous demand for high quality semiconducting, ferroelectric, piezoelectric, oxide single crystals. Since there is a vast market for solid state devices, effort has been made in recent years on producing large size, good quality single crystals. Nowadays the growth of single crystals has assumed great impetus due to their importance both for academic research and technology. GaAs is now used in the area of microwave devices, high speed digital integrated circuits and as substrates for epitaxial layer growth to fabricate photonic and electronic devices. With the recent advance of mobile communication and digital telephony there has been an increasing demand of semi insulating GaAs.
InP is used as the base material for opto-electronic components in long distance fibre optic telecommunications.

Crystal growth is an inter disciplinary subject covering physics, chemistry, electrical engineering, metallurgy, material science, crystallography, mineralogy, etc. In the recent years, direct visualization at atomic resolution of nucleic acid and variety of proteins with which it interacts is possible by growing single crystals. Crystallography is concerned with the nature of the regular atomic arrangements within the crystal. Crystallographers had made remarkable studies about the crystals before the discovery of X-rays by crystals. However, only after that, it became possible to know about the internal arrangement of atoms in the crystals, in a more developed way.

As there was a remarkable achievement in the study of internal atomic arrangements it lead to the study of more physical properties. This interest shifted from the study of natural crystals to the laboratory grown crystals. Progress in crystal growth and epitaxy technology is highly useful for the production of high efficiency photovoltaic cells and detectors for alternative energy and medicine.

1.2. Formation of Crystals

One of the important phenomenon in crystal growth is nucleation. When few atoms or molecules join together in a saturated system a change in energy takes place in the formation of the cluster. The cluster consisting of such atoms or molecules is normally termed as 'embryo'. It may grow or
disintegrate and disappear completely. If the embryo grows to a particular size (critical size) then it is known as ‘critical nucleus’, then there is a greater probability to grow. Thus in crystal growth, the birth of the crystal is an important event. There are four stages involved in the formation of stable nucleus.

a) The first stage is the development of supersaturated stage. This may occur due to a chemical reaction, changes in pressure, temperature or any other chemical or physical conditions.

b) The second stage is the generation of an embryo. It may be either homogeneous when the atoms or molecules build themselves in the interior of the parent system or heterogeneous where the molecules build up on an impurity atom or dust particles on the surface of the container or on any other imperfection.

c) The third stage is the growth of the embryo from the unstable or metastable state to the stable state or to the critical size.

d) The fourth stage is the relaxation process where the texture of the newly born nucleus alters.

The total free energy of a crystal in equilibrium with its surrounding at constant temperature and pressure would be a minimum for a given volume. Since the volume free energy per unit volume is a constant, the critical nucleus will not have a regular morphology of a crystal since it normally contains few tens of atoms or molecules. Under such condition, the critical nucleus can be assigned spherical shape. When a crystal nucleus attains a critical size then it grows into crystal of macroscopic dimension with well developed faces.
In general, in any crystal growth processes the following steps are involved:

1. Generation of reactants,
2. Transport of reactants to the growth surface,
3. Adsorption at the growth surface,
4. Nucleation,
5. Growth,
6. Removal of unwanted reaction products from the growth surface, etc.

The driving force for crystallization is the supersaturation of the gas or liquid phase with respect to the component whose growth is required. Too little saturation will result in an unacceptably slow growth rate. Larger saturation results in non-uniform cellular or dendritic growth. The object for good crystal growth is therefore to achieve and maintain a constant level of supersaturation within this range.

Crystal growth generally takes place when a liquid either solidifies or is saturated to a point where it can no longer retain dissolved material. Further growth can be proceeded when the environment deposits nutrients on the faces that can grow parallel to themselves. Crystals need not be perfect always. The disturbances of structures due to environmental conditions and previous history are the major reasons for this. There are different classes and systems of crystals.
In crystals the atomic array is periodic. In single crystal the periodicity extends throughout the material. In polycrystalline crystal the periodicity does not extend throughout the crystal but is interrupted at grain boundaries. Grains or crystallites are larger than the size of the pattern unit which forms the periodicity. The size of the grains in which the structure is periodic may vary from macroscopic dimensions to several angstroms.

As R.A. Laudise puts it, the term single crystal is difficult to define but is usually thought of as a crystallite that has either been found in nature, separated from polycrystalline mass, or deliberately prepared. The crystallite should be of size sufficient for the esthetic, technological or scientific purpose for which it is intended.

Single crystals find important uses in research. They are almost always required for the determination of any conductivity dependent property in a semiconductor. Single crystals are often required in optical studies. The existence of lasers and masers has created severe new demands for single crystals for research and applications.

1.2.1. Crystal growth methods

The crystal growth may be classified depending upon the nature of the starting materials. Hence the growth of a crystal may proceed by any one of the following methods:
i) Solid growth process involving
   \[ \text{Solid} \rightarrow \text{Solid phase transformation} \],

ii) Melt growth process involving
    \[ \text{Liquid} \rightarrow \text{Solid phase transformation (freezing)} \],

iii) Vapour growth process involving
     \[ \text{Gas} \rightarrow \text{Solid phase transformation (condensation)} \], and

iv) Solution growth process involving
    \[ \text{Solution} \rightarrow \text{Solid phase transformation (precipitation)} \]

In each category of growth methods there are numerous variations, some of which are very specific to particular requirements. The selection of any crystal growth method depends much on the properties of the materials to be crystallized and to a greater extent on the growth kinetics, requirements, such as size, shape, purity, economics, etc.

Crystal growth

(i) From solution (ii) from vapour (iii) from solid (iv) from melt

(i) From Solution

Aqueous solution growth, Gel growth, Organic solution growth, Flux solution growth, Molten metal solution growth, Electro crystallization
Among the above mentioned crystal growth methods, melt growth methods are of the best methods to grow high quality large size single crystals.

1.2.2. Literature available

There are a very large number of published articles, books, and proceedings of schools and conferences on the various aspects of crystal growth theory and practice. Some of the general books to read or dip into are by: Brice [1], Buckley [2], Hartman [3], Gilman [4], Mullin [5], Pamplin [6], Santhana Raghavan and Ramasamy [7], Laudise [8], Peiser [9], Markov [10], etc.
1.3. Alkali Halide Mixed Crystals

Mixed crystals are those of materials chemically similar in nature and having same crystal structure. The mixed crystals are formed from a homogeneous growth of one component in another occupying interstitial or substitutional positions. The mixed crystals can be formed among substances which have similar crystalline structure. There is difference between mixed crystals and doped crystals. If a foreign material is added in small quantity in ppm level to the parent material and the crystal is grown, the crystal is called a doped crystal. When one material is mixed with another material in a large proportion and the crystal is grown, then the crystal is called a mixed crystal. In the mixed crystal the ions are distributed at random throughout the lattice so that the term ‘solid solution’ is more appropriate.

1.3.1. Classification

There are three different kinds of solid solutions namely substitutional, interstitial and defect solid solutions (see Figure 1). In substitutional solid solutions, some of the normal lattice sites in the solvent crystal are occupied by the solute atoms and the structure of the solvent remain unchanged.

Interstitial solid solutions are formed when the solute atoms occupy positions in the interstices of the crystal lattice of the solvent. In defect solid solutions, some sites in the lattice of one of the components remain vacant. Defect solid solutions are formed typically in chemical compounds of transition elements, as well as, sulphides, selenides and some oxides.
Solid solutions. (a) Solvent (b) Substitutional solid solution (c) Interstitial solid solution (d) Defect solid solution.

Fig. 1: Figure showing different types of solid solutions
1.3.2. Various conditions for the formation of mixed crystals

Types of binding: The formation of the mixed crystal required that the bonds in the two crystals be of similar type.

Compounds of the same structure: The ability of two substances to form a solid solution is determined primarily by geometrical considerations. If the two substances are the same, and if the radii of the substituent atoms differ by not more than about 15% from that of the smaller one, a wide range of solid solutions can be expected at room temperature. At higher temperatures a somewhat greater degree of tolerance between the radii is permitted, but if the radius difference exceeds the limit of 15% only a restricted solid solution occurs.

Compounds of different structure: Many examples are known of partial solid solutions between compounds with different crystal structures, and also between compounds of quite different chemical conditions.

There are some difficulties in growing mixed crystals. When two compounds are fused together, a solid solution may or may not be formed according to their phase equilibrium. If an eutectic mixture is formed then we cannot get the mixed crystal. Therefore, consideration of phase equilibrium is very important in growing mixed crystals.
1.3.3. Growth of mixed crystals

There is an increasing demand for crystal of complex composition, comprising of mixed and doped materials. Growth of single crystals of poly component system is a bit complicated process and hence a crystal grower has to tackle several problems such as evaluating, understanding and utilizing the phase relations between the constituents taking part in the growth process.

There are various techniques by which mixed crystals can be grown. Few materials such as Al-Ag, Cu-Zn, Fe-Ni have been grown by strain annealing process. Among many techniques available for the growth of single crystals, Bridgman and Stockbarger methods (melt techniques) are very often used by crystal growers particularly for mixed crystals and doped crystals. According to R. Krishnasamy this method is more suitable for Cd$^{2+}$, Pb$^{2+}$ and Ca$^{2+}$ doped crystals of alkali halides. Mixed crystals of NaCl and KCl (eutectic) are grown by Ingla, S.G. and Ghedekar, S.R. Mixed crystals of CdS – MnS are grown by Komura, Kondo and Mitsuhasi by Bridgman technique. R. Gobinathan and P. Ramasamy have grown mixed crystals of lead iodide and cadmium iodide. V. Hari Babu and U.V. Subba Rao have grown the binary mixed crystals KBr-KCl, NaCl-KCl, KBr-KI, NaCl-NaBr and studied their characteristics. KCl-KBr mixed single crystals have been grown by P. Kumaravelu et al by travelling zone melting technique.

1.3.4. Characterization of mixed crystals

The characterization of mixed crystals involves estimation of the nature (including phase) and the extend of
the components present (stoichiometry). In one component system, stoichiometry is not needed; only crystallinity and defects have to be characterized. The characterization of mixed crystals presents some problems and one has to go through systematically all the available tools before selecting a method. Physical, chemical, X-rays or spectroscopic method is suitable for the characterization of all mixed crystals.

In the case of mixed crystals of KI and AgI the atomic absorption spectroscopy is not satisfactory. In the case of cesium chloride and copper chloride, there are two possible phases CsCuCl$_3$ and CsCuCl$_4$ and hence chemical and physical methods are not satisfactory. It can be characterized by X-ray powder diffraction method. In the case of Pb$^{2+}$ doped NaCl, the characterization is mainly done by atomic absorption spectroscopy, if the dopant level is of the order of ppm.

The other nonunique nature of characterization involves qualitative estimation of crystallinity by the microscopic study of the surface features, etch patterns, and defect density calculation. Molar volume theory is used in the treatment of mixed crystals. The adoptability of a particular method of characterization depends on the component ratio, the phase in which it is present and the interference from the other present impurities, the dilution effect and the tolerance allowed for dopant. The acceptability of chemical, physical, X-ray or spectroscopic method depends on these factors and one has to choose the method carefully so that unambiguous results can be obtained within the tolerance specified.
A mixed crystal has physical properties analogous to those of the pure crystals. The composition dependence varies from system to system and from property to property. In many cases, the property changes monotonically with composition in a linear or nearly linear manner. In a few properties the composition dependence is highly non-linear and in some cases the magnitude of the physical property for the mixed crystal even exceeds the values for the end members. Mixed crystals have found applications as information storage devices, as laser window materials and as neutron monochromators.

1.3.5. Alkali halide mixed crystals

The alkali halides exist in one of the two structures known as NaCl structure and CsCl structure (see Figure 2). These two structures are among the simplest of crystal structures. These crystals are highly ionic and they grow easily and most of them are stable. These crystals have attracted a great deal of attention from experimental as well as theoretical workers and considerable information is available on their various properties.

The solid solutions of alkali halides indeed constitute a very interesting system for optical information storage studies. The alkali halides have played an important role from the beginning of solid state physics. When X-ray diffraction was discovered by Laue (1911) NaCl (rock salt) was one of the first crystals chosen for the famous Laue spot experiment. When Debye (1912) developed his theory of specific heat of solids he applied to metals, but among the non metallic
Unit cells of (a) NaCl and (b) CsCl lattices; • Na (or Cs) and ○ Cl

Fig. 2: Structure of (i) NaCl and (ii) CsCl
solids he chose to apply it to KCl. During 1913 Debye developed the first theory for the interest of thermal vibrations of solids on the X-ray intensities and included KCl among the first crystals to which the theory was applied.

Most alkali halides are water soluble and all have sharp melting points. Over the decades, methods have been developed to grow large clear single crystals either from solution or by solidification of the melt. Good clear large single crystal of alkali halides are available commercially. A number of datas are available on different physical properties like dielectric constant, conductivity, refractive index, thermal parameters, etc [11–18].

The alkali halides are mutually soluble either fully or partially. This give rise to the class of materials called alkali halide mixed crystals or solid solutions. In general, the physical properties of mixed crystals are intermediate between the properties of the two end members. Tobolsky [16] showed that for ionic crystals like alkali halides complete miscibility is possible only above a temperature $T$ given by $T = 4.56\delta^2$, $\delta$ being the percentage difference in lattice constants. For alkali halides, at room temperature, $\delta$ takes a value of 8%.

In view of overall performance of the alkali halides there has been continuing activity in all aspects of alkali halides - crystal growth, generation of physical property data, theories of ionic crystals and applications. A number of review articles have appeared exclusively dealing with alkali halides. Refractive indices of alkali halides [17]; Melting of alkali halides [18];
Growth and characterization of alkali halide mixed crystals [11]; Physical properties of alkali halide mixed crystals [12]; etc. Apart from these a very large number of papers have been published.

In India some of the Research Centres like IISC Bangalore, IIT Delhi, Madras and Kharagpur have studied the different aspects of alkali halides such as Debye-Waller factors, ionic conductivity, dielectric constants, colour centers, etc. Osmania, Kakatiya, Agra, etc universities were undergoing research on alkali halides in the aspects like crystal growth, Debye-Waller factors, ionic conductivity, lattice dynamics, etc. of mixed crystals and pure ones. Alkali halides are useful in infrared transmission. Doped alkali halide crystals make them useful as radiation detectors.

1.3.6. Growth and composition determination

Growth and characterization of alkali halide mixed crystals have been reviewed in detail by Hari Babu and Subba Rao (1984) [11]. Veeresham et al [19] have grown single crystals of mixed crystal systems KCl-KBr, KCl-KI, KBr-KI and KCl-NaCl. In all these systems the dislocation density increases with degree of mixing and is maximum at the equimolar composition. Subba Rao and Hari Babu [20 – 21] studied the micro hardness of KCl-KBr and KBr-KI systems and found that the composition variation is similar to that of dislocation densities. They identified that the mixed crystals have a larger mechanical strength. Padiyan and Mohanlal [22] have grown quaternary mixed crystals of K_{0.5} Rb_{0.5} Cl_{0.5} Br_{0.5}. Mahadevan and his co-workers [14] have grown (NaCl)$_x$(KCl)$_{0.9-x}$(KBr)$_{0.1}$ crystals
from aqueous solutions and the crystals are found to be very stable. Kumar et al [23] grew KBr-KI mixed crystals by the melt method using Czochralski pulling method and studied the properties of the crystal. Geethakrishna grew mixed crystals of NaCl-NaBr and KI-RbI systems by using the pulling method [24]. When the mixed crystals are grown by using the melt technique the difference between starting mixture and resulting crystal is very less when compared to the solution method [12]. For alkali halide mixed crystals with anionic substitution, the method of potentiometric titration can be used for composition determination [20]. It is one of the reliable methods for composition determination. Nair and Walker [25] determined the composition of KCl-KBr mixed crystals from the measured macroscopic densities assuming an additive rule. Using lattice constants the composition of the crystal can be estimated by Vegard's law [26]. There are some other methods like Compton scattering of gamma rays [27] are also used for composition analysis.

1.3.7. Lattice parameters

The accurate determination of the lattice parameters of crystalline materials has assumed certain importance in the recent decades. Results of such studies find application in many aspects of solid state physics. Lattice parameters are required for the calculation of other physical properties such as lattice energy, refractive index, etc.

The lattice parameters of the solid solution KCl$_x$Br$_{1-x}$ have been measured by Havigburst et al [28] and Oberlies [29].
Slagle and McKinstry [30] studied lattice parameters for KCl-KBr solid solutions. Subba Rao [31] determined the lattice parameters of various compositions of KCl_xKBr_{1-x} mixed crystals using Debye-Scherrer powder method. Cohen's method [32] was employed to get the best value of lattice parameters. They observed a linear variation with composition suggesting that the Vegard's law is obeyed. They used the values for microhardness calculations.

The lattice parameters for K_{1-x}Rb_xI single crystals were measured by Van Den Bosch et al [33] at room temperature. They observed that the maximum relative deviation from linearity was \(-0.005\%\) which was much smaller than the variation coefficient. The lattice parameters of pure KI was measured and reported by Swanson and Tatge [34]. They observed a value of 7.066Å. From this Van Den Bosch [33] concluded that the lattice parameters of K_{1-x}Rb_xI at room temperature do not show a non linear behaviour.

The lattice parameters of KBr-KI system was determined by Indira Nair and Walker [35] for KBr_{1-x}I_x mixed crystals by using the conventional Debye-Scherrer method. The lattice parameter variations of KBr-KI with composition is shown in Figure 3. The average composition indicated was determined by chemical methods [35]. The straight line was Vegard's law joining the lattice parameters of KI and KBr for which the values obtained are 7.005 and 6.575Å respectively.

The composition dependence of lattice constants in a mixed crystal series can be expressed by a general relation of the type
Fig. 3: Lattice constant variation of KBr-KI mixed crystals with composition
\[ a_n = x a_1^n + (1-x) a_2^n \] \hspace{1cm} (1)

Different values have been proposed for the exponent \( n \). When \( n = 1 \), equation 1 becomes

\[ a = x a_1 + (1-x) a_2 \] \hspace{1cm} (2)

The above equation (2) is called Vegard's law which predicts a linear composition dependence [26]. When considering the volumes to be additive, we have

\[ a^3 = x a_1^3 + (1-x) a_2^3 \] \hspace{1cm} (3)

This is called as Retger's rule and represents an ideal for mixed crystals [12].

Several investigators have tried to fit their data to one of the three equations explained above. Sirdeshmukh and Srinivas have explained [12] in detail about KCl-KBr (KCl\(_x\)Br\(_{1-x}\)) and K\(_x\)Rb\(_{1-x}\)I lattice constant values. Mahapatra and Pandhi [36] obtained the lattice constants for KCl-KBr system by a novel method. Sahayashajan et al [14] studied the lattice variation of NaCl-KCl-KBr crystals.

### 1.3.8. Thermal parameters

The reduction of intensity of a diffracted x ray or neutron beam due to thermal vibrations in the diffracting crystal is given by

\[ I = I_0 \exp (-2B \sin^2 \theta / \lambda) \]

The Debye-Waller factors of alkali halides have received considerable interest. The available data on Debye-
Waller factors of compound crystals have been compiled together by Butt et al [37] and this compilation includes the work on alkali halides. The compilation by Bult et al includes results on fourteen alkali halides. The compilation shows that different numbers of the alkali halide group have received different degrees of alternation and thirteen cited reports on KCl.

In the alkali halides the heavier of the two atoms has smaller B value. Wasastjerna [38], Meisalo and Inkinen [39], Tompson [40] and Shepard et al [41] studied Debye-Waller factors of KBr.

Regarding the Debye-Waller factor of mixed crystals of alkali halides Wasastjerna studied [42] KCl-KBr system from X-ray intensities. Mohanlal et al [43] determined the Debye-Waller factors of KCl-KBr for two compositions. They identified that the Debye-Waller factors of mixed crystals are larger than those expected from additivity. The Debye-Waller factors in the equimolar region are larger than that for end members. Srinivas and Sirdeshmukh [44] studied Debye-Waller factors of KCl-RbCl. Srinivas and Sirdeshmukh [45] studied KBr-RbBr system for the Debye-Waller factor. They identified that the composition dependence is non-linear. Hussain et al [46] determined the Debye-Waller factors of KBr-KI system. Beg et al studied for KI-Rbl system [47]. Geethakrishna et al [13] determined the Debye-Waller factors of mixed crystals of alkali halides such as KxRb_{1-x}I and NaClxBr_{1-x} systems.

The Debye temperatures for the mixed and pure alkali halide crystals were found out from the Debye-Waller
factors of the above mentioned system. The Debye temperature is derivable from experimental data like specific heats, elastic constants, X-ray and neutron diffraction intensities [48-49].

The Debye temperature of KCl-KBr system was found out from specific heats [50], elastic constants [51-52], etc by several authors. The Debye temperatures of KBr-KI were determined from elastic constants [36] and specific heat values [53]. Using X-ray diffraction intensity data, the Debye temperature of KBr-RbBr [45] were determined. Debye temperatures of KI-RbI system [47] were determined by using neutron diffraction data. The Debye temperatures of K_xRb_(1-x)I systems were studied by Geethakrishna et al [13]. The results obtained by Geethakrishna et al identified that the Debye temperature shows slight non-linear composition dependence with negative deviation from linearity. It is established that the Kopp-Neumann law provides [54] the best fit with experimental values. The Kopp-Neumann relation is

$$\theta^3 = x\theta_1^3 + (1-x)\theta_2^3.$$  

where $\theta$ is the Debye temperature of the mixed crystal and $\theta_1$ and $\theta_2$ are that of the end members.

1.3.9. D.C. conductivity measurements

The considerable interest devoted to the transport processes in ionic crystals during the last few decades led to very important results. Alkali halides hold a predominating place.

Ionic conductivity studies provide valuable information on the state of point imperfections. Conduction in ionic crystals
is a defect controlled property. The defect concentration increases exponentially with the rise of temperature and the electrical conductivity increases correspondingly.

Ionic conductivity measurements as a function of temperature have been done by number of workers on pure alkali halides doped with anion and cation impurities [11]. Though an extensive amount of work has been done on pure and doped alkali halide crystals, the work on mixed alkali halides is very limited. As conduction in alkali halides occurs by motion of vacancies, the alkali halide mixed crystals should then exhibit good electrical conductivity compared with pure end components.

Ambrose and Wallace [55] studied the electrical conductivity of KCl-KBr crystals in the temperature range of 400 to 540°C. They observed that the conductivity of mixed crystals was found to be never far outside the range of conductivity fixed by the pure components. Annenkov and Grishukov [56] studied the electrical property of solid solutions of alkali-halogen compounds of the KCl-KBr system. They observed that the value of conductivity increases exponentially with increase in temperature. They calculated the activation energy from the slope of the temperature-conductivity plot.

Schultze [57] studied the ionic conductivity measurements on solid solutions of KCl-KBr systems. The conductivity was found to increase gradually as the concentration of KBr increases in the case of KCl-KBr mixed crystals and attains a maximum at an intermediate position. The activation
energies were also calculated and observed that, it decreases as composition increases in KBr in the KCl-KBr mixed crystals [58-59].

The conductivity measurements on KBr-KI mixed crystals revealed the fact that [60] as the composition of KI in KBr increases the conductivity gradually increases and attains maximum at an intermediate composition of 60 mole % KI in KBr and also the conductivity decreases on either side of mole % KI in KBr. The conductivity in KBr was found to be more as compared to KI and different composition of mixed crystals. The behaviour was found to be different as compared to that observed in KCl-KBr system. Also, the variation of conductivity with composition was found to be non-linear attaining maximum value at an intermediate composition. The activation energy calculated in both the regions showed a non-linear variations with composition.

Kumar et al [23] studied the KBr-KI mixed crystals. They observed that the conductivity of KI is higher than KBr and also in the mixed crystals of various compositions, the values of conductivity increases as temperature increases. The conductivity appears to reach maximum in the crystal containing 70% of KI in KBr. However, the conductivity of KBr_xI_{1-x} mixed crystals is always larger than that of pure KBr.

1.3.10. Dielectric measurements

The dielectric constant is one of the basic electrical properties of solids. The measurement of dielectric constant and
loss as a function of frequency and temperatures is of interest both from theoretical point of view and from applied aspects.

The dielectric behaviour of these alkali halide crystals has also been investigated by several workers. Measurements have been done at room temperature, low temperatures and to some extent at elevated temperatures. The pressure dependence of dielectric constant has also been investigated in some cases.

Dielectric studies on KCl, KBr and KI have been carried out by a number of workers. Robinson and Hallet studied [61] dielectric constant of KCl and KBr. Lowndes and Martin [62], Kamiyoshi and Nigara [63], Andeen et al [64] and Mahmud et al [65], studied the dielectric constant of KCl and KBr crystals at low temperature and room temperature. Sathaiah [6] determined the dielectric parameters such as dielectric constant and dielectric loss of KCl and KBr crystals.

Lowndes [67] and Chandra [68] have investigated the dielectric properties of KI crystals at room temperature. Mahmud et al [65] investigated the dielectric properties of KI crystals with 1KHz frequency. Kamiyoshi and Nigara [63] studied with 1 MHz for KI crystals.

There is very little work reported on the dielectric constant of mixed crystals. Fertel and Perry [69] were the first to determine the static dielectric constants of the KCl-KBr systems. Kamiyoshi and Nigara [70] studied for the same system at 1 MHz frequency by the immersion method. Sirdeshmumkh
and Prameela Devi [71] studied the KCl-KBr system. Sathaiah has done a systemic study on KCl-KBr system [66] for various composition at a frequency of 100 KHz. He investigated the dielectric properties of the above mixed crystal and identified a non-linear variation with different composition values and also a sharp increase on $\varepsilon_r$ at higher temperatures. The dielectric losses ($\tan \delta$) of KCl-KBr system were also determined.

Kamiyoshi and Nigara [70] have carried out dielectric studies on KBr-KI system and identified that the composition dependence of dielectric constant is slightly non-linear with positive deviation from linearity.

No report is available on ternary mixed crystals till now.

1.4. Present Work

Simple crystal structure and bonding scheme of alkali halides (typical examples of ionic crystals) have made them favourite candidates for testing theories. Stability and availability in the form of single crystals of meaningful size of these materials have made them the subject of numerous experimental investigations. In the last few decades, the alkali halides have also proved useful in several applications ranging from infrared optical windows to continuous wave tunable lasers.

The alkali halides are mutually soluble either fully or partially which give rise to the class of materials called the alkali halide mixed crystals or solid solutions. In general, the
physical properties of mixed crystals are intermediate between the properties of the end members which creates the possibility of having tailor-made crystals with desired characteristics. Similarly, impurities can be introduced into an alkali halide crystal during its growth resulting in a 'doped' crystal which provided another method to have tailor-made crystals. Generally, these doped crystals have properties close to, but not exactly the same as, the host crystal.

Use of alkali halides is limited by their mechanical softness and hence there arise the need to strengthen them. Alkali halide mixed crystals and doped crystals are generally harder than the pure crystals. Hence, they become more useful. Alkali halide mixed crystals are of the completely disordered substitutional type. Some of these crystals have found applications as information storage devices, as laser window materials and neutron monochromators. Considerable work have been reported on the growth and physical properties of binary mixed crystals of alkali halides [eg. Refs. 11 - 12].

Regarding ternary mixed crystals, the only reported work is by Mahadevan and his co-workers [14]. They have studied the lattice variation in \((NaCl)_x(KCl)_{0.9-x}(KBr)_{0.1}\) crystals grown from aqueous solutions. Their study showed that though the miscibility problem was there \((NaCl)_x(KCl)_{0.9-x}(KBr)_{0.1}\) crystals are more stable than \(Na_xK_{1-x}Cl\) crystals.

A research programme was planned in our laboratory as a systematic approach to this previous study and a series of investigations were undertaken. The present work (a scientific research) forms a part of the above programme.
involving investigations on the growth and characterization of \((\text{NaCl})_x(\text{KBr})_{y-x}(\text{KI})_1 y\) crystals. Mrs. K. Jayakumari has undertaken investigations on the growth and characterization of \((\text{NaCl})_x(\text{KCl})_{y-x}(\text{KBr})_{1-y}\) crystals [72]. Mr. S. Perumal has undertaken investigations on the growth and characterization of \((\text{KCl})_x(\text{KBr})_{y-x}(\text{KCl})_1 y\) crystals [73].

Pure as well as ternary mixed crystals of NaCl, KBr and KI were grown by the melt method.

Density was measured by using the floatation technique. Refractive index was determined by using the Abbe refractometer and Gladstone's rule. Composition of the grown crystals was estimated by using the additive properties of density and refractive index.

X-ray diffraction data were collected from powder samples of crystals using an automated X-ray diffractometer. The reflections were indexed and lattice parameters determined.

Mean Debye-Waller factors were determined from the X-ray powder diffraction intensity data by the Wilson plot method. Other thermal parameters like mean square amplitude of vibration, Debye temperature and Debye frequency were determined using the Debye-Waller factor.

D.C. electrical conductivities were measured by using the two-probe method at various temperatures ranging from room temperature to 150°C. Activation energies and mean jump frequencies were also determined.
Capacitances and dielectric loss tangents were measured using an LCR meter with a fixed frequency of 1KHz at various temperatures ranging from room temperature to 150°C. Dielectric constants, A.C. electrical conductivities and activation energies were determined.

Ultraviolet spectra of all the grown crystals were also recorded using an UV spectrometer and analysed.

A detailed report of this scientific research work is presented in this thesis.

Chapter 2 provides a description of the various methods adopted in the present work for the growth of sample crystals needed for the present study and determination of density, refractive index and composition of the grown crystals. X-ray diffraction data collection on powdered samples of all the crystals grown along with the determination of lattice parameters and thermal parameters like Debye-Waller factor, Debye temperature, mean square amplitude of vibration and Debye frequency from the X-ray powder diffraction data are also dealt. The results obtained are also reported and discussed in the last sections.

The results obtained in our D.C. electrical conductivity and dielectric measurements are reported and discussed in Chapter 3 together with giving a brief description (in each case) of the methods followed in the present study.
Chapter 4 gives a brief description of the ultraviolet spectral studies made.

Summary and conclusions derived out of the present study along with the scope for future work in the same area of research are provided in Chapter 5.

Finally, the literatures cited are listed in the 'REFERENCES' section.