Chapter - 1

Introduction
1. INTRODUCTION

In this Chapter, the actual work done by the author is introduced along with providing some background information related to the present topic of research.

1.1. Introduction

Crystal growth and characterization is an expanding field in material science which is identified as a thrust area of research and the recent developments in technology has stimulated the commercial importance of the subject. The word crystal stems from the Greek word ‘Krystallos’ meaning ‘clear ice’. It was first applied to clear crystals of quartz in the Swiss Alps, because, these were thought to be formed from water under condition of intense cold.

The three general states of matter, viz, gaseous, liquid and solid represent the different degrees of atomic or molecular mobility. In the gaseous state, molecules are in constant, vigorous and random motion. In the liquid state, random molecular motion is much more restricted. In the solid state, molecular motion is confined to an oscillation about a fixed position.

Solids may be crystalline or amorphous. The crystalline state differs from the amorphous state in a regular arrangement of the constituent molecule or ions into some fixed and rigid pattern known as lattice.
A third class of solids called quasi crystals, which contain atoms in ordered arrays, but the patterns they assume are subtle and do not recur at regular intervals. Such patterns are called quasi periodic. Certain organic crystals on heating carefully pass into a state which is intermediate between those of solid and liquid, this state is called the mesomorphic state or liquid crystal.

Modern technology brings a wide variety of applications to crystal. Without crystals there would be no electronic industry, no photonic industry, no fiber optic communication, very little modern optical equipment and some very important gaps in conventional production engineering.

Crystal growth is a controlled phase transformation to solid phase, either from solid or liquid or gaseous state. Alkali halide crystals, because of their scintillation property finds wide applications in radiation detection. The halogenic scintillators are among the most wide spread type of scintillation materials and they are classified as two broad groups; alkali halide scintillators and fluoroperovskites.

Artificial crystals are grown everyday in the laboratory. At present, industries, science and technology hardly make any progress without the development of new materials of enhanced performance. To meet with the increased need of crystals in various fields, scientists have started growing pure as well as mixed and impurity added (doped) crystals (controlled mixing and controlled impurity addition).
1.2. Alkali Halide Crystals

Alkali halide crystals are crystals formed by the combination of alkali atoms of the first group and halogens of the seventh group. The electronic configuration of the alkali atoms and the halogen atoms favour electronic transfer and formation of ions.

The alkali halide crystals crystallize in either of the two structures, viz, the NaCl structure and the CsCl structure (see Figure 1 [1]). In ambient conditions CsCl, CsBr and CsI assume the CsCl structure and the rest crystallize with the NaCl structure.

All the alkali halide crystals, except that of LiF and NaF, are soluble in water and can, in principle, be crystallized from solution. All the alkali halide crystals have congruent melting points and therefore their crystals can be grown from their melts. The alkali halide crystals with NaCl structure have a beautiful cleavage along the (100) plane whereas those with CsCl structure do not exhibit cleavage.

Because of the importance of alkali halides as model crystals and their potential as device materials – purely scientific as well as technological – a vast amount of information has been generated with regard to all aspects of the alkali halides over several decades. Information on alkali halide remain scattered over a large number of journals, books and reference sources. Sirdeshmukh et al [1] have brought together data on a comprehensive range of physical properties of alkali halides under one cover for the use of researchers in the new millennium.
Fig. 1: Unit cells of (a) NaCl and (b) CsCl lattices

[● Na (or Cs) and ○ Cl]
1.3. Methods of Crystal Growth

During the last few decades the growth of bulk crystals has assumed enormous importance for both academic research and technology. Various techniques used for crystal growth range from a small inexpensive technique to a complex sophisticated expensive process and crystallization time ranges from minutes, hours, days to months.

The general principles of crystal growth can be applied almost to all the methods of crystal growth, but the precise way in which one can grow a particular crystal varies from material to material. Based on the nature of the starting material, crystal growth can be classified [2] as:

- Growth from solid → solid - solid phase transformation;
- Growth from liquid → liquid – solid phase transformation;
- Growth from vapour → vapour – solid phase transformation.

A fourth main category may be defined which is already included in the above definition is:

Solution growth → growth of solute from an impure melt.

This is done primarily because solution growth methods differ from methods used for pure melt growth. So we have four main categories of crystal growth techniques: Solid growth, vapour growth, melt growth and solution growth.

Solid growth technique can be considered as the conversion of a polycrystalline material into a single crystal by causing the grain boundaries to be swept through and pushed out of the material due to atomic diffusion. But, this is very slow at ordinary temperature and is only rarely used.
Single crystals of high purity can be grown from the vapour by sublimation and chemical vapour deposition. In this process, the source material to be crystallized is provided from the vapour phase. Main advantage of this method is that it does not involve the contacting of the growing surface with a liquid or solid phase, thus avoiding numerous potential problems during and after the growth process.

Crystal growth from aqueous solution is one of the ancient methods of crystal growth. The major advantage of this method is that it permits crystal growth at a temperature well below the melting point. Depending on the solvents and solubility of the solute, solution growth technique is classified into two as:

(i) Low temperature solution growth; and
(ii) High temperature solution growth.

Melt method is the method employed to grow sample crystals in the present study. Hence, this method is discussed in brief in Chapter 3.

There are a very large number of published books, articles and proceedings of conferences and schools on the various aspects of crystal growth theory and practical. Some of the general books to read or dip into are by: Pamplin (Ed.) [2], Hartman [3], Brice [4], Mullin [5], Sangwal [6], Ramasamy and Santhana Raghavan [7] and Byrappa and Ohachi [8].

1.4. Present Work

Alkali halides are considered as the crystals of highest symmetry [9]. 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 of crystals of meaningful size of these materials have made them the subject of numerous experimental investigations.

In 1946 Seitz [1] remarked “In the field of solids, the properties of alkali halides have an enduring interest, since these crystals have continuously yield to persistent investigation and have gradually provided us with a better and better understanding of the most interesting properties of all solids”. This statement remains relevant even now.

The development of lasers revived the interest in alkali halides as materials for optical components. This led to the development of alkali halide polycrystalline material for use as optical windows. Several recent reports are also available on alkali halide crystals [10-18].

The alkali halides are mutually soluble either fully or partially which gives 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 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 completely disordered substitutional type. Alkali halide crystals have several practical applications as information storage devices, laser host materials, radiation detectors, X-ray and neutron monochromators, and infrared (IR) optical components. In view of this, it becomes necessary and useful to prepare binary, ternary and quaternary mixed crystals regardless of miscibility problem and characterize them by measuring their physical properties.

Haribabu and Subbarao [19] have reviewed the aspects of the growth and characterization of alkali halide mixed crystals. Sirdeshmukh and Srinivas [20] have reviewed the physical properties. Several more reports are available on binary mixed crystals of alkali halides [21-24]. Some reports are also available on ternary and quaternary mixed crystals of alkali halides [25-36]. An updated but a brief review of studies made on alkali halide mixed crystals is presented in Chapter 2 of this thesis. Recently, alkali halide crystals have also been found to be a good medium for preparing II-VI compound nanocrystals [37-39].

For ionic crystals like alkali halides complete miscibility is possible only above a temperature $T^oK$ given by $T = 4.5 \delta^2$, $\delta$ being the percentage difference in lattice constants (Tobolsky's rule) [40]. $\delta$ takes a value of 8% for alkali halides at room temperature. A study of literature has shown that there are broad miscibility gaps observed in several binary systems of alkali halides. NaCl-KCl [41] is an example. Barrett and Wallace [42] determined the lattice parameters of Na$_x$K$_{1-x}$Cl crystals and found that this system does not form a continuous series of single phased mixed crystals. Thompson and Waldbaum [43] have analyzed the two-phase region halite-sylvite in the system NaCl-KCl.
Nair and Walker [44] observed that for the extreme concentration ranges \( x < 0.3 \) and \( x > 0.7 \) the \( \text{KBr}_{1-x}\text{I}_x \) crystals could be characterized by a single f.c.c. lattice parameter, while in the intermediate region three f.c.c. phases characterized by three lattice parameters. Recently, Mahadevan and his co-workers have observed multiple phases in the case of \( (\text{NaCl})_x(\text{KCl})_{y-x}(\text{KBr})_{1-y} \) [32], \( (\text{KCl})_x(\text{KBr})_{y-x}(\text{KI})_{1-y} \) [34], and \( (\text{NaCl})_x(\text{KBr})_{y-x}(\text{KI})_{1-y} \) [35] crystals.

According to Tobolsky's rule, the complete miscibility is possible for NaBr-KBr only above a temperature of 488°K. However, Anandakumari and Chandramani [45] have reported the growth of single phased \( (\text{KBr})_x(\text{NaBr})_{1-x} \) single crystals at room temperature from aqueous solutions. So, it would be interesting to prepare \( \text{Na}_x\text{K}_{1-x}\text{Br} \) crystals from melt and characterize the grown crystals.

The deviation in lattice parameters between NaCl and KBr is 17.017% while the same between NaBr and KCl is only 5.285%. As per the Tobolsky's rule, NaBr and KCl are miscible while NaCl and KBr are not at room temperature. Also, \( \text{Na}^+ \) has more affinity towards Cl than Br. So, it would be interesting to grow multiphased mixed crystals using NaBr and KCl as the starting materials and characterize the grown crystals.

The reports of Boudine and his co-workers [37-39] have inspired to think in new direction as we are interested in discovering new materials. It would be an interesting idea to add ZnS (an interesting divalent semiconductor material) to the alkali halides and prepare crystals by the melt method and characterize the grown crystals.

In the present investigation, several useful studies have been made by us on alkali halide mixed crystals:
(i) Polycrystals of Na$_x$K$_{1-x}$Br have been prepared, for the first time, from melt and characterized;

(ii) Polycrystalline multiphased mixed crystals using the miscible alkali halides, viz. NaBr and KCl have been prepared, for the first time, from melt and characterized;

(iii) Polycrystals of (NaCl)$_{0.5}$(KBr)$_{0.5}$, Na$_{0.5}$K$_{0.5}$Br and the end members, viz. NaCl, NaBr and KBr added with ZnS have been prepared, for the first time, from melt and characterized;

(iv) Polycrystals of the end members, viz. NaCl, NaBr, KCl and KBr have been prepared from melt and characterized for comparison purposes; etc.

All the crystals have been prepared under identical conditions. The prepared crystals have been characterized chemically by determining the bulk composition using the measured density and refractive index values. Some of these were confirmed by atomic absorption spectroscopic (AAS) measurements.

X-ray powder diffraction data were collected using an automated X-ray diffractometer. The reflections were indexed and the lattice parameters determined by using the standard methods.

Mean Debye-Waller factors were determined 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 factors. Compressibilities and mean sound velocities were also determined.

DC electrical conductivities were measured by the conventional two-probe method at various temperatures ranging from 35 to 150°C. Dielectric constant, dielectric loss tangents and AC electrical conductivities were measured by the parallel plate capacitor method with a fixed frequency of 1 kHz at various temperatures ranging from 35 to 150°C. Activation energies and mean jump frequencies were also determined.
In addition, ultraviolet and Fourier transform infrared spectral studies have been carried out on all the grown (prepared) crystals.

The results obtained in the present study indicate that the multiphased mixed crystals prepared are expected to be highly useful. A report of this research work is presented in this thesis.

The thesis is divided into five Chapters together with the 'References' section. Chapter 1 introduces the present research work and Chapter 5 contains the summary, conclusions and scope for the future. A review (though not comprehensive) of various studies made on alkali halide mixed crystals is presented in Chapter 2. Chapter 3 provides the details of materials used and various experimental and other methods followed in the present study. The results obtained are reported along with sufficient discussion in Chapter 4.