1. INTRODUCTION

A brief introduction to the actual work done by the candidate is provided in this Chapter. In addition, a brief non-comprehensive review of various studies made on alkali halide mixed crystals in the near past is provided.

1.1. Crystalline Materials

The atomic aggregates are normally classified into three states of matter, viz. the solid state, the liquid state, and the gaseous state. Materials in the solid state are characterized by definite shape, definite volume, incompressibility, rigidity and mechanical strength. This indicates that the molecules, atoms or ions that make up a solid material are closely packed, they are held together by strong cohesive forces and cannot move at random.

Materials in the solid state are classified into three types, viz. crystalline, amorphous and quasi-crystalline. Liquid crystals are not considered here. These are certain organic crystals which, on heating carefully, pass into a state which is intermediate between those of solid and liquid.

In the solid state there is a tendency of the constituent atoms to arrange themselves in an ordered periodic pattern. A solid material with such a regular periodic arrangement is called as crystalline. A solid material without having a definite
geometrical form is called as non-crystalline or amorphous. Solid materials containing atoms in ordered arrays but the patterns assumed are subtle and not occurring at regular intervals are called as quasi-crystals. We do not consider here amorphous and quasi-crystalline materials.

Crystalline materials are classified into three types, viz. macro crystals, micro crystals, and nano crystals. Macro crystals are ordered crystals of mm (≈10^{-3} m and above) size. They are visible (bulk single) crystals in which the periodicity extends throughout the material and it is free from inner boundaries. Micro crystals are microscopically small (tiny) crystals. Nano crystals are crystals of dimensions ≈10^{-7} m and below.

Crystals having inner boundaries along with external boundary are called as polycrystalline. It is equivalent to the combination of a number of single crystals attached together at some point. If only two crystals are attached together it is called as twinned, if more crystals are together it is called as multiplex. In general, these are called as polycrystalline.

There is a vast market for solid state devices using crystalline materials. Crystalline materials (or crystals) are used in several appliances which are highly useful to the mankind. The requirements of the electronics industry have stimulated many advances in crystal growth, both extending existing techniques and bringing forward new ones. The modern technology is very much dependent upon crystalline materials such as semiconductors, polarizers, transducers, radiation detectors, ultrasonic amplifiers, ferrites, magnetic garnets, solid state lasers and nonlinear optic, piezoelectric,
acoustooptic and photosensitive materials and crystalline films for microelectronics and computer industries. All these involve research in the preparation (formation) and characterization of crystalline materials.

1.2. Alkali Halide Mixed Crystals

Alkali halide compounds are formed by the combination of alkali atoms (Li, Na, K, Rb, and Cs) of the first group (IA) and halogens (F, Cl, Br and I) of the seventh (VII A) group. The alkali halides crystallize either in the NaCl (sodium chloride) structure or in the CsCl (cesium chloride) structure. In ambient conditions CsCl, CsBr and CsI crystallize in the CsCl structure and the others crystallize in the NaCl structure. All the alkali halides (except LiF and NaF) are soluble in water and can (in principle) be crystallized from aqueous solution. All the alkali halides have congruent melting points and therefore their crystals can be formed 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.

In the present study, we consider only three alkali halides, viz. NaCl, NaBr and NaI. Table 1 contains some of the general properties of these [1, 2]. Figure 1 [3] shows the sodium chloride structure as these three alkali halides crystallize in this structure.

Seitz made a statement in 1946 on alkali halides which remains relevant even now.

In the field of solids, the properties of alkali halides have an enduring interest, since these crystals have continuously yielded to persistent investigation and have gradually provided us with a better and better understanding of the most interesting properties of solids.
Table 1: Some of the general properties of NaCl, NaBr and NaI [1, 2]

<table>
<thead>
<tr>
<th>Property/Parameter</th>
<th>NaCl</th>
<th>NaBr</th>
<th>NaI</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular weight (M)</td>
<td>58.45</td>
<td>102.91</td>
<td>149.92</td>
</tr>
<tr>
<td>Colour</td>
<td>Colourless</td>
<td>White</td>
<td>White</td>
</tr>
<tr>
<td>Density (d) (g/cc)</td>
<td>2.1617</td>
<td>3.1997</td>
<td>3.6714</td>
</tr>
<tr>
<td>Refractive index (n, measured at λ = 5893 Å)</td>
<td>1.5443</td>
<td>1.6412</td>
<td>1.7745</td>
</tr>
<tr>
<td>Melting point (T_m) (°C)</td>
<td>801</td>
<td>747</td>
<td>661</td>
</tr>
<tr>
<td>Boiling point (T_b)(°C)</td>
<td>1465</td>
<td>1447</td>
<td>1304</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Cubic</td>
<td>Cubic</td>
<td>Cubic</td>
</tr>
<tr>
<td>Lattice type</td>
<td>f.c.c.</td>
<td>f.c.c.</td>
<td>f.c.c.</td>
</tr>
<tr>
<td>Space group</td>
<td>Fm3m</td>
<td>Fm3m</td>
<td>Fm3m</td>
</tr>
<tr>
<td>Point group</td>
<td>m3m</td>
<td>m3m</td>
<td>m3m</td>
</tr>
<tr>
<td>Coordination number</td>
<td>6</td>
<td>6</td>
<td>6</td>
</tr>
<tr>
<td>Number of molecules per unit cell</td>
<td>4</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>Lattice constant (a) (Å)</td>
<td>5.6402</td>
<td>5.9772</td>
<td>6.4728</td>
</tr>
<tr>
<td>Structure type</td>
<td>NaCl</td>
<td>NaCl</td>
<td>NaCl</td>
</tr>
<tr>
<td>Interionic distance (r) (Å)</td>
<td>2.8200</td>
<td>2.9865</td>
<td>3.2364</td>
</tr>
<tr>
<td>Molar volume (V_M) (cm³)</td>
<td>27.012</td>
<td>32.083</td>
<td>40.829</td>
</tr>
<tr>
<td>Molecular volume (V_m) (Å³)</td>
<td>44.854</td>
<td>53.274</td>
<td>67.798</td>
</tr>
<tr>
<td>Compressibility (ψ) (x10⁻¹² cm²/dyne)</td>
<td>4.17</td>
<td>5.02</td>
<td>6.64</td>
</tr>
<tr>
<td>Mean sound velocity (V) (km/s)</td>
<td>2.848</td>
<td>2.108</td>
<td>1.728</td>
</tr>
<tr>
<td>Property/Parameter</td>
<td>NaCl</td>
<td>NaBr</td>
<td>NaI</td>
</tr>
<tr>
<td>--------------------------------------------------------</td>
<td>---------------</td>
<td>---------------</td>
<td>---------------</td>
</tr>
<tr>
<td>Mean Debye-Waller factor (B) (Å²)</td>
<td>1.53(2)</td>
<td>1.23(15)</td>
<td>1.94(25)</td>
</tr>
<tr>
<td>Debye temperature (K)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>From X-ray/neutron diffraction (θ_m)</td>
<td>278(2)</td>
<td>202(6)</td>
<td>144(6)</td>
</tr>
<tr>
<td>From elastic constants (θₑ)</td>
<td>322</td>
<td>224</td>
<td>167</td>
</tr>
<tr>
<td>From compressibility (θᵥ)</td>
<td>292</td>
<td>241</td>
<td>210</td>
</tr>
<tr>
<td>Microhardness (H_,) (kg/mm²)</td>
<td>0.216</td>
<td>0.129</td>
<td>0.101</td>
</tr>
<tr>
<td>Static dielectric constant (ε(0)) (for 1 kHz frequency at 300 K)</td>
<td>5.8949</td>
<td>6.3957</td>
<td>-</td>
</tr>
<tr>
<td>Electronic dielectric constant (εₑ) (at 290 K)</td>
<td>2.33</td>
<td>2.60</td>
<td>3.01</td>
</tr>
<tr>
<td>Activation energy of ionic conduction (W) (eV)</td>
<td>0.83</td>
<td>0.80</td>
<td>0.60</td>
</tr>
<tr>
<td>Solubility in water (S) (g per 100 g of solvent)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>At 30°C</td>
<td>36.1</td>
<td>98.4</td>
<td>191</td>
</tr>
<tr>
<td>At 40°C</td>
<td>36.4</td>
<td>107</td>
<td>205</td>
</tr>
</tbody>
</table>
Figure 1: Unit cell of NaCl lattice

[● Na and ● Cl]
A vast amount of information has been generated with regard to all aspects of alkali halide crystals over several decades due to their importance as model crystals and their potential as device materials. 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. Alkali halide crystals have proved useful in several applications which range from X-ray monochromators to tunable lasers. The development of lasers revived the interest in alkali halides as materials for optical components which led to the development of alkali halide polycrystalline material for use as optical windows. Several recent reports are also available on simple and doped alkali halide crystals [4-70]. Recently, Boudine and his co-workers [71-73] have found that the alkali halide crystals can act as a good medium for the preparation of II-VI compound nanocrystals.

Two elements or compounds are said to form a continuous solid solution (mixed crystal) if single lattice parameter can be assigned to the solid solution at all compositions. In the continuous solid solutions of alkali halides, Retger's rule (additivity of molar volumes) [74] and Vegard's law (linear variation of lattice parameter with composition) [75] are closely followed as indicated by X-ray diffraction studies.

There are three different kinds of solid solutions (mixed crystals), viz. substitutional, interstitial, and defect solid solutions (see Figure 2) [76]. In substitutional solid solutions, some of the normal lattice sites in the solvent crystal are occupied by solute atoms, and the structure of the solvent remains unchanged. Interstitial solid solutions are formed when the solute atoms occupy positions in the interstices of the
Figure 2: Different types of solid solutions
[ (a) Solvent; (b) Substitutional solid solution;
(c) Interstitial solid solution; (d) Defect solid solution]
crystal lattice of the solvent. In defect solid solutions, some sites in the lattice of one of
the components remain vacant.

The formation of a mixed crystal requires that:

(i) the structures of the two crystals should be of similar type;
(ii) the bonds in the two crystals should be of similar type;
(iii) the radii of the substituent atoms should not differ by more than about 15% from
that of the smaller one; and
(iv) the difference between their lattice parameters should be less than 6%.

A mixed crystal, in general, has physical properties analogous to those of the end
member (pure) crystals. The composition dependence varies from system to system and
property to property. The property changes, in many cases, monotonically with
composition in a linear or nearly linear manner. Once the trend in composition
dependence is established, we have a means to have a tailor-made crystal with a desired
value for a given property. In some properties, the composition dependence is highly
nonlinear. In some other cases, the magnitude of the physical property for the mixed
crystal even exceeds the values for the end members. In these cases, it is as if we have a
new crystal in the family. This behaviour is shown in the microhardness of alkali halide
mixed crystals. In a few cases, mixed crystals show exciting behaviour. An example of
this is the appearance of a first-order Raman spectrum in mixed crystals of alkali halides
which is absent in the pure alkali halide (end member) crystals.

Alkali halide mixed crystals are of completely disordered substitutional type.
Interesting and important as the alkali halides are, no less important are their mixed
crystals. Use of alkali halides is limited by their mechanical softness and hence there arise the need to strengthen them. Alkali halide mixed crystals are found to be harder than the end member crystals and are more useful in applications. In addition, alkali halide mixed crystals find their applications in optical, opto-electronic and electronic devices.

Tobolsky [77] showed that for ionic crystals like alkali halides, complete miscibility is possible only above a particular temperature $T^0K$ given by $T = 4.5 S^2$, where $S$ being the percentage deviation in the lattice parameter. For alkali halides, $S$ takes a value of 6% at room temperature. A study of literature has shown that there are broad miscibility gaps observed in several binary and ternary systems of alkali halides. NaCl-KCl [78-80] and KBr-KI [81] are examples of binary systems. NaCl-KCl-KBr [82, 83], KCl-KBr-KI [84, 85], and NaCl-KBr-KI [86, 87] are examples of ternary systems.

Haribabu and Subbarao [88] have reviewed the aspects of the growth and characterization of alkali halide binary mixed crystals. Sirdeshmukh and Srinivas [89] have reviewed the physical properties of alkali halide binary mixed crystals. Several more reports are also available on binary mixed crystals of alkali halides [90-100]. However, only few reports are available on ternary and quaternary mixed crystals (including multiphased and doped ones) of alkali halides [82-87, 101-109]. A brief (non-comprehensive) review of various studies made on alkali halide mixed crystals in the near past is presented here. Ternary and higher level (both single phased and multiphased) mixed crystals are mainly considered. As few reviews are already available on binary mixed crystals, they are given less importance here.
The composition (x) dependence of lattice constants in a mixed crystal series can be expressed by a general relation of the type,

\[ a^n = x a_1^n + (1-x) a_2^n. \]  \hfill (1)

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

\[ a = x a_1 + (1-x) a_2. \]  \hfill (2)

This predicts a linear composition dependence. This was suggested empirically by Vegard and is now known as Vegard's law [75].

If the volumes are assumed to be additive, we get

\[ a^3 = x a_1^3 + (1-x) a_2^3. \]  \hfill (3)

This is known as Retger's rule [74]. This represents an ideal mixed crystal. Durham and Hawkins [110] also, through theoretical investigation, predicted that n = 3.

Zen [111] pointed out that if the difference in lattice constants is very small, equation (3) becomes indistinguishable from equation (2). Slagle and Mckinstry [112] obtained n = 3.26 for KCl-KBr mixed crystals.

In order to describe the composition (x) dependence of Debye temperature of binary mixed crystals several relations have been proposed [113]. Assuming the additivity of specific heats and assuming the Debye theory expression for specific heat at low temperatures (the Debye \( T^3 \) expansion) Kopp-Neumann [114] obtained the relation

\[ \Theta^3 = x \Theta_1^3 + (1-x) \Theta_2^3, \]

where \( \Theta_1 \) and \( \Theta_2 \) are the Debye temperatures for the end member crystals and \( \Theta \) is that of the mixed crystal. Nagaiah and Sirdeshmukh [115], following the same procedure but employing the high temperature expression for specific heat, obtained the relation
\[ \theta^2 = x\theta_1^2 + (1-x)\theta_2^2 \]

Karlsson [116] and Nagaiah and Sirdeshmukh [115] respectively proposed, from empirical considerations, the following relations:

\[ \theta^2 = x\theta_1^{-2} + (1-x)\theta_2^{-2}, \]

\[ \text{and } \theta^{-1} = x\theta_1^{-1} + (1-x)\theta_2^{-1}. \]

Geetakrishna et al [94] studied this aspect with seven alkali halide mixed systems and found that these seven systems satisfied the Kopp-Neumann relation for the Debye temperatures.

Mahadevan and his co-workers [101] initiated the studies on ternary mixed crystals of alkali halides. They obtained larger and more stable single crystals from \((\text{NaCl})_x(\text{KCl})_{0.5-x}(\text{KBr})_{0.1}\) solutions than from \(\text{Na}_x\text{K}_{1-x}\text{Cl}\) solutions. Although the miscibility problem was there, their study has illustrated that a KBr addition to NaCl-KCl system may yield a new class of stable materials.

Later, a single phase behaviour was found by Mijangos et al [105] in a crystal obtained by growing it with a mixture containing four single alkali halides, given a quaternary crystal. \(\text{KCl-KBr-RbCl-RbBr}\) that was studied in two molar concentrations of each single component, being the starting point to obtain four different types of ternary mixed crystals and the known binary mixed crystals, conforming to a crystallographic family. \(\text{KCl-KBr-RbCl}\) was the first one studied finding that it behaves as a single phase [103]. Mijangos et al [107] have concluded that their results showed that the ternary compound doped with europium is a promising material that could be interesting to future research about the luminescent and dosimetric processes in double doped ternary...
systems with europium and other divalent metallic impurities that in single alkali halide crystals and cesium halide crystals were well studied [117-124].

Recently, Jayakumari and Mahadevan [82, 83] have grown single crystals of \((\text{NaCl})_x(\text{KCl})_{y-x}(\text{KBr})_{1-y}\) for various values of \(x\) and \(y\) by the Czochralski method. Refractive indices and densities of all the crystals were determined and also used for the estimation of the bulk composition in the crystal. The observed lattice parameters showed the existence of two phases (each nearly corresponds to NaCl and KCl-KBr) in crystals with NaCl content greater than 0.1 mole fraction. Thermal parameters like Debye-Waller factor (\(B\)), mean square amplitude of vibration (\(<u^2>\)), Debye temperature (\(\theta_D\)) and Debye frequency (\(f_D\)) were determined from the X-ray powder diffraction data. These parameters show a highly nonlinear composition dependence. AC and DC electrical measurements indicate that the bulk composition has nonlinear influences on the electrical parameters. Table 2 contains the lattice parameters and Debye temperatures together with initial (taken for crystallization) and final (estimated) compositions.

Perumal and Mahadevan [84, 85] have grown single crystals of \((\text{KCl})_x(\text{KBr})_{y-x}(\text{KI})_{1-y}\) for various values of \(x\) and \(y\) and characterized by carrying out density, refractive index, X-ray diffraction, and AC and DC electrical measurements. The thermal and electrical parameters are found to have nonlinear influences with the bulk composition. X-ray diffraction analysis indicates that the mixed crystals have two f.c.c. phases each nearly corresponds to KCl-KBr and KI. Lattice parameters and Debye temperatures together with initial (taken for crystallization) and final (estimated) compositions are provided in Table 3.
<table>
<thead>
<tr>
<th>System (with composition taken for crystallization)</th>
<th>Lattice parameters (Å)</th>
<th>Debye temperature θ(K)</th>
<th>System (with estimated composition)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>For NaCl phase</td>
<td>For mixed phase</td>
<td></td>
</tr>
<tr>
<td>(NaCl)<em>{0.1}(KCl)</em>{0.7}(KBr)_{0.2}</td>
<td>-</td>
<td>6.3672</td>
<td>193.4</td>
</tr>
<tr>
<td>(NaCl)<em>{0.2}(KCl)</em>{0.6}(KBr)_{0.2}</td>
<td>5.6547</td>
<td>6.3806</td>
<td>223.8</td>
</tr>
<tr>
<td>(NaCl)<em>{0.3}(KCl)</em>{0.5}(KBr)_{0.2}</td>
<td>5.6357</td>
<td>6.3715</td>
<td>202.2</td>
</tr>
<tr>
<td>(NaCl)<em>{0.4}(KCl)</em>{0.4}(KBr)_{0.2}</td>
<td>5.6558</td>
<td>6.3874</td>
<td>215.7</td>
</tr>
<tr>
<td>(NaCl)<em>{0.5}(KCl)</em>{0.3}(KBr)_{0.2}</td>
<td>5.6587</td>
<td>6.4082</td>
<td>214.6</td>
</tr>
<tr>
<td>(NaCl)<em>{0.6}(KCl)</em>{0.2}(KBr)_{0.2}</td>
<td>5.6310</td>
<td>6.4218</td>
<td>216.8</td>
</tr>
<tr>
<td>(NaCl)<em>{0.7}(KCl)</em>{0.1}(KBr)_{0.2}</td>
<td>5.6167</td>
<td>6.4609</td>
<td>203.2</td>
</tr>
<tr>
<td>(NaCl)<em>{0.8}(KCl)</em>{0.1}(KBr)_{0.2}</td>
<td>-</td>
<td>6.3829</td>
<td>174.7</td>
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<tr>
<td>(NaCl)<em>{0.2}(KCl)</em>{0.4}(KBr)_{0.4}</td>
<td>5.6196</td>
<td>6.2679</td>
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<td>(NaCl)<em>{0.3}(KCl)</em>{0.3}(KBr)_{0.4}</td>
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<td>6.4217</td>
<td>219.0</td>
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<td>(NaCl)<em>{0.4}(KCl)</em>{0.2}(KBr)_{0.4}</td>
<td>5.6215</td>
<td>6.4480</td>
<td>229.6</td>
</tr>
<tr>
<td>(NaCl)<em>{0.5}(KCl)</em>{0.1}(KBr)_{0.4}</td>
<td>5.6177</td>
<td>6.4839</td>
<td>181.4</td>
</tr>
<tr>
<td>(NaCl)<em>{0.6}(KCl)</em>{0.1}(KBr)_{0.4}</td>
<td>-</td>
<td>6.4082</td>
<td>183.1</td>
</tr>
<tr>
<td>(NaCl)<em>{0.6}(KCl)</em>{0.3}(KBr)_{0.5}</td>
<td>5.5985</td>
<td>6.4356</td>
<td>181.0</td>
</tr>
<tr>
<td>(NaCl)<em>{0.7}(KCl)</em>{0.2}(KBr)_{0.5}</td>
<td>5.6043</td>
<td>6.4598</td>
<td>198.5</td>
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<tr>
<td>(NaCl)<em>{0.8}(KCl)</em>{0.1}(KBr)_{0.5}</td>
<td>5.6084</td>
<td>6.4759</td>
<td>182.6</td>
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<tr>
<td>(NaCl)<em>{0.9}(KCl)</em>{0.1}(KBr)_{0.6}</td>
<td>-</td>
<td>6.4519</td>
<td>225.0</td>
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<tr>
<td>(NaCl)<em>{0.2}(KCl)</em>{0.2}(KBr)_{0.6}</td>
<td>5.5642</td>
<td>6.4785</td>
<td>185.7</td>
</tr>
<tr>
<td>(NaCl)<em>{0.3}(KCl)</em>{0.1}(KBr)_{0.6}</td>
<td>5.6064</td>
<td>6.4959</td>
<td>176.5</td>
</tr>
<tr>
<td>(NaCl)<em>{0.4}(KCl)</em>{0.1}(KBr)_{0.8}</td>
<td>-</td>
<td>6.5202</td>
<td>190.5</td>
</tr>
</tbody>
</table>

Table 2: Lattice parameters and Debye temperatures together with the initial and final compositions for \((\text{NaCl})_x(\text{KCl})_y(\text{KBr})_{1-y}\) crystals [82].
Table 3: Lattice parameters and Debye temperatures together with the initial and final compositions for (KCl)$_x$(KBr)$_{y-x}$(KI)$_{1-y}$ crystals [85].

<table>
<thead>
<tr>
<th>System (with composition taken for crystallization)</th>
<th>Lattice parameters (Å)</th>
<th>Debye temperature (K)</th>
<th>System (with estimated composition)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(KCl)$<em>{0.1}$(KBr)$</em>{0.7}$(KI)$_{0.2}$</td>
<td>6.8689  6.5087</td>
<td>162.4</td>
<td>(KCl)$<em>{0.285}$(KBr)$</em>{0.471}$(KI)$_{0.244}$</td>
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<td>(KCl)$<em>{0.2}$(KBr)$</em>{0.6}$(KI)$_{0.2}$</td>
<td>6.9000  6.4440</td>
<td>173.4</td>
<td>(KCl)$<em>{0.425}$(KBr)$</em>{0.257}$(KI)$_{0.318}$</td>
</tr>
<tr>
<td>(KCl)$<em>{0.3}$(KBr)$</em>{0.5}$(KI)$_{0.2}$</td>
<td>6.9282  6.4017</td>
<td>170.2</td>
<td>(KCl)$<em>{0.481}$(KBr)$</em>{0.188}$(KI)$_{0.331}$</td>
</tr>
<tr>
<td>(KCl)$<em>{0.4}$(KBr)$</em>{0.4}$(KI)$_{0.2}$</td>
<td>6.9435  6.3377</td>
<td>169.3</td>
<td>(KCl)$<em>{0.590}$(KBr)$</em>{0.040}$(KI)$_{0.370}$</td>
</tr>
<tr>
<td>(KCl)$<em>{0.1}$(KBr)$</em>{0.3}$(KI)$_{0.4}$</td>
<td>6.9386  6.4184</td>
<td>152.9</td>
<td>(KCl)$<em>{0.395}$(KBr)$</em>{0.147}$(KI)$_{0.458}$</td>
</tr>
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<td>(KCl)$<em>{0.2}$(KBr)$</em>{0.4}$(KI)$_{0.4}$</td>
<td>6.9507  6.4610</td>
<td>155.3</td>
<td>(KCl)$<em>{0.364}$(KBr)$</em>{0.159}$(KI)$_{0.477}$</td>
</tr>
<tr>
<td>(KCl)$<em>{0.3}$(KBr)$</em>{0.3}$(KI)$_{0.4}$</td>
<td>6.9571  6.3761</td>
<td>161.8</td>
<td>(KCl)$<em>{0.440}$(KBr)$</em>{0.080}$(KI)$_{0.480}$</td>
</tr>
<tr>
<td>(KCl)$<em>{0.4}$(KBr)$</em>{0.2}$(KI)$_{0.4}$</td>
<td>6.9290  6.3404</td>
<td>160.9</td>
<td>(KCl)$<em>{0.499}$(KBr)$</em>{0.031}$(KI)$_{0.470}$</td>
</tr>
<tr>
<td>(KCl)$<em>{0.1}$(KBr)$</em>{0.3}$(KI)$_{0.6}$</td>
<td>6.9447  6.4441</td>
<td>135.6</td>
<td>(KCl)$<em>{0.224}$(KBr)$</em>{0.114}$(KI)$_{0.662}$</td>
</tr>
<tr>
<td>(KCl)$<em>{0.2}$(KBr)$</em>{0.2}$(KI)$_{0.6}$</td>
<td>6.9353  6.3780</td>
<td>134.7</td>
<td>(KCl)$<em>{0.257}$(KBr)$</em>{0.064}$(KI)$_{0.679}$</td>
</tr>
<tr>
<td>(KCl)$<em>{0.3}$(KBr)$</em>{0.1}$(KI)$_{0.6}$</td>
<td>6.9439  6.3446</td>
<td>138.6</td>
<td>(KCl)$<em>{0.283}$(KBr)$</em>{0.023}$(KI)$_{0.694}$</td>
</tr>
<tr>
<td>(KCl)$<em>{0.1}$(KBr)$</em>{0.1}$(KI)$_{0.8}$</td>
<td>6.9493  6.3804</td>
<td>123.4</td>
<td>(KCl)$<em>{0.155}$(KBr)$</em>{0.035}$(KI)$_{0.810}$</td>
</tr>
</tbody>
</table>
Selvarajan and Mahadevan [86, 87] have grown polycrystals of (NaCl), (KBr)$_{y-x}$ (Kl)$_{1-y}$ for various values of x and y and characterized by carrying out density, refractive index, X-ray diffraction and AC and DC electrical measurements. X-ray diffraction analysis indicates that the mixed crystals have three f.c.c. phases each nearly corresponds to NaCl, KBr and Kl. The thermal and electrical parameters are found to have nonlinear influences with the bulk composition. Lattice parameters and Debye temperatures together with initial (taken for crystallization) and final (estimated) compositions are given in Table 4.

A novel spatially coherent crystalline nanocomposite obtained from a melt of KBr, RbCl, RbBr, Kl and Rbl salts was characterized by Mijangos and his co-workers [108]. This material consists of an aggregation of crystallites, ranging from 5 to 100 nm in size, of three different f.c.c. phases. One of these phases was identified as single RbBr, another one was discussed to be the binary mixed Kl (39%) : Rbl (61%) phase, and the third one was discussed to be the ternary mixed KBr (47%) : RbCl (39%) : RbBr (14%) phase. The measured unit-cell sizes for these phases are 6.889 (7), 7.234 (25) and 6.631 (5)Å, respectively. The crystal lattices of the crystallites forming the composite, no matter the particular phase they belong to, are spatially coherent to each other so that the normal vector to a particular lattice (hkl) plane, in different crystallites, are confined in the space within a narrow circular cone around the lattice [hkl] direction.

Very recently, Padma and Mahadevan [109] have reported the possibility of preparing multiphased binary, ternary, etc mixed alkali halide crystals using the miscible NaBr and KCl as the starting materials. The crystals were characterized by X-ray diffraction, density and refractive index measurements. Table 5 contains the densities,
Table 4: Lattice parameters and Debye temperatures together with the initial and final compositions for (NaCl)$_x$(KBr)$_{y-x}$(KI)$_{y}$ crystals [86].

<table>
<thead>
<tr>
<th>System (with composition taken for crystallization)</th>
<th>Lattice parameters (Å)</th>
<th>Debye temperature (K)</th>
<th>System (with estimated composition)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>For NaCl phase</td>
<td>For KBr Phase</td>
<td>For KI phase</td>
</tr>
<tr>
<td>(NaCl)$<em>{0.1}$(KBr)$</em>{0.8}$(KI)$_{0.1}$</td>
<td>5.6700</td>
<td>6.5210</td>
<td>6.9810</td>
</tr>
<tr>
<td>(NaCl)$<em>{0.3}$(KBr)$</em>{0.6}$(KI)$_{0.1}$</td>
<td>5.5985</td>
<td>6.5453</td>
<td>6.9450</td>
</tr>
<tr>
<td>(NaCl)$<em>{0.5}$(KBr)$</em>{0.4}$(KI)$_{0.1}$</td>
<td>5.5690</td>
<td>6.4970</td>
<td>6.8590</td>
</tr>
<tr>
<td>(NaCl)$<em>{0.7}$(KBr)$</em>{0.2}$(KI)$_{0.1}$</td>
<td>5.5960</td>
<td>6.4860</td>
<td>6.9150</td>
</tr>
<tr>
<td>(NaCl)$<em>{0.1}$(KBr)$</em>{0.6}$(KI)$_{0.3}$</td>
<td>5.5630</td>
<td>6.5730</td>
<td>6.9380</td>
</tr>
<tr>
<td>(NaCl)$<em>{0.3}$(KBr)$</em>{0.4}$(KI)$_{0.3}$</td>
<td>5.5880</td>
<td>6.5260</td>
<td>6.8820</td>
</tr>
<tr>
<td>(NaCl)$<em>{0.5}$(KBr)$</em>{0.2}$(KI)$_{0.3}$</td>
<td>5.5910</td>
<td>6.5280</td>
<td>6.9502</td>
</tr>
<tr>
<td>(NaCl)$<em>{0.1}$(KBr)$</em>{0.4}$(KI)$_{0.5}$</td>
<td>5.6530</td>
<td>6.4910</td>
<td>6.9080</td>
</tr>
<tr>
<td>(NaCl)$<em>{0.3}$(KBr)$</em>{0.2}$(KI)$_{0.5}$</td>
<td>5.5260</td>
<td>6.5090</td>
<td>6.9090</td>
</tr>
<tr>
<td>(NaCl)$<em>{0.1}$(KBr)$</em>{0.2}$(KI)$_{0.7}$</td>
<td>5.9810</td>
<td>6.5100</td>
<td>6.9500</td>
</tr>
</tbody>
</table>
Table 5: Density, refractive indices and lattice parameters together with initial and final compositions for mixed crystals grown from NaBr and KCl [109]

<table>
<thead>
<tr>
<th>System (with composition taken for crystallization)</th>
<th>Density (g/cc)</th>
<th>Refractive index</th>
<th>Lattice parameters (Å)</th>
<th>System (with estimated composition)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>For NaCl phase</td>
<td>For NaBr phase</td>
</tr>
<tr>
<td>(NaBr)<em>{0.2}(KCl)</em>{0.8}</td>
<td>2.1808</td>
<td>1.5153</td>
<td>5.6310</td>
<td>-</td>
</tr>
<tr>
<td>(NaBr)<em>{0.4}(KCl)</em>{0.6}</td>
<td>2.4021</td>
<td>1.5395</td>
<td>5.6383</td>
<td>-</td>
</tr>
<tr>
<td>(NaBr)<em>{0.5}(KCl)</em>{0.5}</td>
<td>2.4713</td>
<td>1.5498</td>
<td>5.6388</td>
<td>-</td>
</tr>
<tr>
<td>(NaBr)<em>{0.6}(KCl)</em>{0.4}</td>
<td>2.6290</td>
<td>1.5689</td>
<td>5.6830</td>
<td>5.8826</td>
</tr>
<tr>
<td>(NaBr)<em>{0.8}(KCl)</em>{0.2}</td>
<td>2.9632</td>
<td>1.6061</td>
<td>5.6367</td>
<td>5.8625</td>
</tr>
</tbody>
</table>
refractive indices and lattice parameters together with initial (taken for crystallization) and final (estimated) compositions.

In the case of mixed crystals, the composition dependence of physical properties find an important place while carrying out the growth and characterization studies on them. Therefore, accurate determination of the composition is important.

In the case of ternary mixed crystals, there are two unknowns (x and y) to be determined which limits the use of powerful techniques like atomic absorption spectroscopy to determine accurately only the metal atom contents and not the individual alkali halide components present.

Mahadevan and his co-workers [82, 85, 86, 109] have developed a method to determine the two unknowns (x and y) by using the measured density and refractive index values. It has been found that the density and refractive index values form a linear relationship with composition for the binary mixed crystals [89]. Assuming that these values have a linear relationship with composition for the ternary mixed crystals also, the following relations may be written:

\[ d = x d_1 + (y-x) d_2 + (1-y) d_3; \]
\[ n = x n_1 + (y-x) n_2 + (1-y) n_3. \]

Here, \( d, d_1, d_2 \) and \( d_3 \) represent the densities of mixed crystal, first component, second component and third component, respectively; \( n, n_1, n_2 \) and \( n_3 \) represent the refractive indices of mixed crystal, first component, second component and third component, respectively. By solving the above two equations for \( x \) and \( y \) values composition of the ternary mixed crystal can be determined.
The composition dependence of lattice parameters in a ternary mixed crystal series may be expressed by a general relation of the type

$$a^n = xa_1^n + (y-x)a_2^n + (1-y)a_3^n.$$

When the volumes are assumed to be additive, we get

$$a^3 = xa_1^3 + (y-x)a_2^3 + (1-y)a_3^3.$$

This is the Retger's rule extended to ternary mixed crystals representing an ideal ternary mixed crystal. This is not really accurate or appropriate especially in the case of multiphased ternary mixed crystals for calculating the lattice parameters in these systems.

In the case of multiphased crystals, the total average values of lattice parameters were used for the comparison.

In the case of ternary mixed crystals, the Debye temperatures show a nonlinear variation with composition, deviating highly (except for few crystals) from the Kopp-Neumann relation extended to ternary mixed crystals:

$$\theta^3 = x\theta_1^3 + (y-x)\theta_2^3 + (1-y)\theta_3^3.$$

It is even less than that of the component alkali halides in some cases. This happens because of the enhancement of Debye-Waller factor which may be attributed to the increase in vibrational entropy due to mixing.

1.3. Present Work

Now, we are in a position to understand the importance of alkali halide mixed crystals (both single phased and multiphased). They 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.

The sodium halides, viz. NaCl, NaBr and NaI are approximately miscible and can be expected to form single phased ternary mixed crystals. NaI is highly deliquescent and hence is very less stable. But, when forming mixed crystals, it is expected to obtain more stable materials.

In the present study, polycrystals of (NaCl)$_x$(NaBr)$_y$(NaI)$_{1-y}$ without and with adding CdS have been grown (prepared or formed), for the first time, from melt and characterized. Polycrystals of the components, viz. NaCl, NaBr and NaI have also been grown from melt and characterized for comparison purposes. A total of 20 crystals (14 mixed and 6 others) have been grown under identical conditions.

The grown crystals were characterized chemically by determining the bulk composition using the measured density and refractive index values. The Cd content was determined by atomic absorption spectroscopic (AAS) measurements.

X-ray diffraction (XRD) data for the powdered samples were collected using an automated X-ray diffractometer. The reflection data were indexed and the lattice parameters were determined by using the available standard methods. In the case of (NaCl)$_x$(NaBr)$_y$(NaI)$_{1-y}$ crystals (without adding CdS), thermal parameters like Debye-Waller factor, mean square amplitude of vibration, Debye temperature and Debye frequency were also determined from the XRD (integrated) intensity data.
The dielectric parameters like dielectric constant, dielectric loss tangent and AC electrical conductivity were measured by the parallel plate capacitor method with a fixed frequency of 1 kHz at various temperatures ranging from 40 – 150°C. The DC electrical conductivity was measured by the conventional two-probe method at various temperatures ranging from 40-150°C. Activation energies were also determined.

A report of the present research work is provided in this thesis. The present research work has already been introduced here. A brief review of various studies made on alkali halide mixed crystals in the near past has already been added here in this Chapter (Chapter 1). Chapter 2 contains the details of the growth of crystals along with estimation of the bulk composition. Details of XRD measurements along with the results obtained are provided in Chapter 3. The methods followed in the electrical measurements together with the results obtained are provided in Chapter 4. Chapter 5 contains the summary and conclusions. Chapter 6 contains the scope for future research work in the same direction.