2. GROWTH OF CRYSTALS

A brief description of the method used for the growth of crystals in the present study is provided in this Chapter. Also provided here is a brief description of the determination of density, refractive index and composition of all the crystals grown. In addition, the results obtained from these experiments are reported and discussed.

2.1. Formation of Crystals

Crystal formation (growth) is a controlled phase transformation to ordered solid phase, either from solid or liquid or gaseous phase. The growth units, namely the atoms or molecules, diffuse to the growth site from the mother phase, when given sufficient time to get orderly arranged on the lattice.

Crystal formation needs the careful control of a phase change. If the crystal is in a dynamic equilibrium with its parent phase the free energy is at a minimum and no growth will occur. For the crystal formation to occur this equilibrium must be disturbed by a change of the correct sign in temperature, pressure, chemical potential (e.g. saturation), electrochemical potential (e.g. electrolysis), or strain. The system may then release energy to its surrounding to compensate for the decrease in entropy occasioned by the ordering of atoms in the crystal and the evolution of heat of crystallization. In a well-
designed growth process just one of these parameters is held minimally away from its equilibrium value to provide a driving force for the crystal formation.

Crystal formation then is a non-equilibrium process and thought must be given to the temperature and concentration and other gradients and the fact that heat of crystallization is evolved and must be removed to the surroundings. At the same time the crystal growth process must be kept as near equilibrium and as near to a steady state process as possible. This is why control of the crystal growth environment and a consideration of growth kinetics both at the macroscopic and atomic levels are of vital importance to the success of a crystal growth experiment.

Three main categories of crystal growth methods may be defined:

Growth from the solid : $S \rightarrow S$ processes involving solid – solid phase transitions;

Growth from the melt : $L \rightarrow S$ processes involving liquid – solid phase transitions;

Growth from the vapour : $V \rightarrow S$ processes involving vapour– solid phase transitions.

One more category may be defined which is strictly already included in the above definitions:

Solution growth : growth of solute from an impure melt.

The above category is separately defined primarily because growth from the melt is such a large and important category and because solution growth methods differ from methods used for pure melt growth.
For bulk growth of high quality single crystal material seeded melt growth (e.g. crystal pulling or float zone melting) (crystal formation from melt) is undoubtedly the best technique available for congruently melting materials. If a material is wanted in thin film form with accurately controlled doping, composition and quality on available substrate material as in the semiconductor and photonics industries, vapour deposition (crystal formation from vapour), especially chemical vapour deposition or molecular beam epitaxy, is an appropriate method, although sometimes solution growth is preferred. In other cases solution growth (crystal formation from solution) is the next best choice—using a seed crystal if possible. This is a particularly useful technique of obtaining small crystals of new materials for scientific research. The conditions cannot readily be chosen—they are fixed by the system.

A large number of published articles, books and proceedings of schools and conferences on the various aspects of crystal (macro, micro and nano) formation theory and practice. Some of the general books which give useful informations are by: Hartman [125], Pamplin (Edn.) [126], Brice [127], Mullin [128], Sangwal [129], Santhana Raghavan and Ramasamy [130], Byrappa and Ohachi [131], Chopra and Kaur [132] and Nalwa (Edn.) [133].

2.2. Growth of Sample Crystals

Formation of crystals from melt is a method of crystal growth, which relates to solids, which can be melted and crystallized. This is also the method which is widely employed for materials which melt congruently and have manageable vapour pressures at their melting points. Polycrystals of alkali halides are highly useful as components in
optical devices [1]. Mahadevan and his co-workers [86, 109] have grown polycrystalline samples of ternary mixed crystals of alkali halides and found that the crystals grown are macroscopically compact and can be cut into required shapes and polished.

In the present study the crystals were grown by adopting the methods followed by Mahadevan and his co-workers [86, 109]. Photograph of the equipment used for the growth of crystals in the present study is shown in Figure 3.

2.2.1. Growth of (NaCl)$_x$(NaBr)$_{y-x}$(NaI)$_{1-y}$ crystals

Analytical reagent (AR) grade samples of NaCl, NaBr and NaI were used as the starting materials for the growth of crystals.

100 g of the substance, weighed according to the molecular ratio by weight, was thoroughly mixed and was taken in a silica crucible. The amount of substance in grams for preparing the required samples of composition given by (NaCl)$_x$(NaBr)$_{y-x}$(NaI)$_{1-y}$ may be obtained by using the following formula.

\[ P \times \frac{x \times \text{molecular weight of NaCl} + (y-x) \times \text{molecular weight of NaBr} + (1-y) \times \text{molecular weight of NaI}}{x \times \text{molecular weight of NaCl} + (y-x) \times \text{molecular weight of NaBr} + (1-y) \times \text{molecular weight of NaI}} = 100 \]

Weight of NaCl to be taken = \( P \times x \times \text{molecular weight of NaCl} \)

Weight of NaBr to be taken = \( P \times (y-x) \times \text{molecular weight of NaBr} \)

Weight of NaI to be taken = \( P \times (1-y) \times \text{molecular weight of NaI} \)
Figures 3: Photograph of equipment used for the growth of crystals
The crucible was kept inside a muffle furnace (capable of heating up to 1200°C) having a temperature controller (accuracy is ± 1°C) and heated till the whole substance was melted. The temperature was further increased to 850°C and kept at this temperature for 1 hr for homogeneous mixing to take place due to convection. The molten liquid was then gradually cooled. A total of seven crystals \([(\text{NaCl})_x(\text{NaBr})_y(\text{NaI})_{1-x-y}] \) with \(x\) having the values of 0.1, 0.3 and 0.5 and \(y\) having the values of 0.6 and 0.8] were grown by the above method and under identical conditions. The end member crystals (NaCl, NaBr and NaI) were also grown for comparison purposes. NaI is less stable (due to deliquescence) and is expected to cause the mixed crystals less stable. Hence, mixed crystals with NaI component upto 0.4 only were grown and characterized.

### 2.2.2. Growth of CdS added crystals

Analytical reagent (AR) grade samples of NaCl, NaBr, NaI and Cds were considered as the starting materials. The crystals grown were NaCl:Cds, NaBr:Cds, NaI:Cds and \((\text{NaCl})_x(\text{NaBr})_y(\text{NaI})_{1-x-y}:\text{Cds}\) [Seven crystals with \(x\) having the values of 0.1, 0.3 and 0.5 and \(y\) having the values of 0.6 and 0.8]. Amount of alkali halide (pure or mixed) taken was 100 g and that of Cds taken was 10 g. Both were mixed properly in an agate mortar and transferred to the crucible and melted. The melting point of Cds was high (1750°C [134]), however, it homogeneously dispersed in the alkali halide melt. The crystals were grown in a way similar to that followed for the growth of alkali halide ternary mixed and end member crystals.

### 2.3. Estimation of Bulk Composition

Bulk composition of the crystals grown in the present study were determined by following the methods used by Mahadevan and his co-workers [82, 85-86, 109].
Densities of all the grown crystals were determined to an accuracy of $\pm 0.008$ g/cc by using the flotation method [135-138]. Carbon tetrachloride of density 1.594 g/cc and bromoform of density 2.890 g/cc were used as the lower and higher density liquids respectively. For the crystals having density higher than that of bromoform the density was measured by finding the mass and volume of rectangular shaped crystals.

Refractive index of an undersaturated solution of the crystal in distilled water was measured using an Abbe refractometer. Refractive index of the crystal (to an accuracy of $\pm 0.006$) was determined by using the Gladstone's rule [139-142]:

$$
\frac{(n-1)d}{P} = \frac{(n_1-1)d_1}{P_1} + \frac{(n_2-1)d_2}{P_2}
$$

where $n$, $n_1$ and $n_2$ represent the refractive indices of solution, solvent and solute (crystal) respectively. $d$, $d_1$ and $d_2$ are the densities of solution, solvent and solute respectively. $P$, $P_1$ and $P_2$ are the percentage weights of solution, solvent and solute respectively.

It has been found that the density and refractive index values form linear relationships with bulk composition for the binary mixed crystals [89]. They are:

$$
\begin{align*}
\text{d} & = \text{xd}_1 + (1-x)\text{d}_2; \text{ and} \\
\text{n} & = \text{xn}_1 + (1-x)\text{n}_2.
\end{align*}
$$

Here, $d$, $d_1$ and $d_2$ represent the densities of mixed crystal and that of the constituent end member crystals respectively. Assuming that these values form linear relationships with composition for the ternary mixed crystals also, the following relations may be written:

$$
\begin{align*}
\text{d} & = \text{xd}_1 + (y-x)\text{d}_2 + (1-y)\text{d}_3; \text{ and} \\
\text{n} & = \text{xn}_1 + (y-x)\text{n}_2 + (1-y)\text{n}_3.
\end{align*}
$$

Here, $d$, $d_1$, $d_2$, $d_3$, $n$, $n_1$, $n_2$ and $n_3$ have the usual meaning as in the case of binary systems. Bulk composition of the grown ternary mixed crystals were estimated by
solving the above two equations for x and y values. The atomic absorption spectroscopic measurements were carried out to determine the Cd$^{2+}$ contents in CdS added crystals. Details of this are presented in Section 2 of Chapter 3.

2.4. Results Obtained

All the twenty crystals grown in the present study are polycrystalline in nature. However, macroscopically they are found to be compact and can be cut into required shapes and polished. Photograph of (NaCl)$_{0.3}$(NaBr)$_{0.3}$(NaI)$_{0.4}$ crystal grown is shown in Figure 4 as an illustration. The mixed crystals grown are found to be less transparent and less deliquescent (i.e. more stable) when compared to the end member crystals.

Normal microhardness measurements were not carried out on the crystals grown in the present study since they are polycrystalline in nature. However, to have some idea on the relative hardness of the end member and mixed crystals grown, rough scratching test (although this method is a crooked one) was done with fingers. The scratching was done with more care especially to avoid the variation in finger pressure. The mixed crystals were found to be harder than the end member crystals.

At temperatures nearer to the freezing point (temperature at which the solidification takes place) the crystals were observed (with the help of a torch light) to be fairly transparent. When the crystals were cooled from high temperature to the room temperature (in about 12 hrs time) the transparency of the crystals reduced and became white. This may be partly due to the introduction of thermal defects since the rate of cooling was not constant (it is a sort of natural cooling only). Another reason is related to the incorporation of natural impurities present in the starting materials used for the growth of crystals.
Figure 4: Photograph of $(NaCl)_{0.3}(NaBr)_{0.3}(NaI)_{0.4}$ crystal grown
The dominant impurities present in NaCl are halides (bromide and iodide, 0.005%), potassium (0.01%), insoluble matter (0.003%) and divalent ions (barium 0.001%, calcium 0.002% and magnesium 0.002%). The dominant impurities present in NaBr are chloride (0.6%), sulphate (0.05%) and iron (0.001%). The dominant impurities present in NaI are moisture (3%), sulphate (0.03%) and potassium (0.1%).

No specific controls were provided to prevent these impurities from entering the crystals. The concentrations of impurities “dissolved” in the lattice increases as the temperature of the crystal increases. If for a certain temperature \( T \) the concentration of impurities is higher than allowable due to the solubility limit, then the substance excess precipitates to form a new phase-the precipitate [143]. The level of natural impurities present in the starting materials used in the present study is expected to cause precipitation effects even in the end member crystals (NaCl, NaBr and NaI).

In the case of CdS added crystals, brown colouration takes place with significant intensity. Figure 5 illustrates this. Also, the CdS added crystals grown are found to be more hard, more stable and less transparent when compared to the pure simple and mixed alkali halide crystals.

The depth profile study has not been carried out for all the CdS added alkali halide crystals. However, in order to understand the effect of CdS addition along the crystal, the depth profile study has been carried out only on \((\text{NaCl})_{0.7}(\text{NaBr})_{0.1}(\text{NaI})_{0.2} : \text{CdS}\) crystal. In all the characterization studies, the depth profile was made by making the measurements for three different samples taken from top, middle and bottom portions. Sample taken from the middle portion was considered for measurements in the case of other nineteen crystals.
Figure 5: Photographs of CdS added
$\text{(NaCl)}_{0.5}\text{(NaBr)}_{0.3}\text{(NaI)}_{0.2}$ crystal
The observed density and refractive index of all the \((\text{NaCl})_x(\text{NaBr})_y(\text{NaI})_{1-x}\) as well as end member (pure) crystals are provided in Table 6. Observed density and refractive index of the end member crystals compare well with those reported in the literature [1] (reported values are given in brackets). Composition of the starting material and estimated bulk composition of the grown crystals are also provided in Table 6. The bulk composition (taken for crystallization) dependence of density and refractive index are shown (as an illustration) in Figures 6 and 7 respectively.

Density and refractive index have been found to be linearly dependent with bulk composition in several binary mixed alkali halide crystals [89]. Variation of density and refractive index with bulk composition is found to be nearly linear for the present ternary mixed crystals also. This indicates that the linear dependence of these properties is not only true for binary mixed systems but also for ternary mixed alkali halide crystals.
Table 6: Densities and refractive indices together with the initial and final compositions for \((\text{NaCl})_x(\text{NaBr})_y(\text{NaI})_{1-x}\) crystals. Values reported in the literature are given in brackets.

<table>
<thead>
<tr>
<th>System (with composition taken for crystallization)</th>
<th>Density (g/cc)</th>
<th>Refractive index</th>
<th>Estimated composition in the crystal</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCl</td>
<td>2.152 (2.1614)</td>
<td>1.5402 (1.5443)</td>
<td>NaCl</td>
</tr>
<tr>
<td>NaBr</td>
<td>3.183 (3.1997)</td>
<td>1.6334 (1.6412)</td>
<td>NaBr</td>
</tr>
<tr>
<td>NaI</td>
<td>3.630 (3.6714)</td>
<td>1.7625 (1.7745)</td>
<td>NaI</td>
</tr>
<tr>
<td>((\text{NaCl})<em>{0.1}(\text{NaBr})</em>{0.7}(\text{NaI})_{0.2})</td>
<td>3.195 (3.6714)</td>
<td>1.657 (1.7745)</td>
<td>((\text{NaCl})<em>{0.094}(\text{NaBr})</em>{0.717}(\text{NaI})_{0.189})</td>
</tr>
<tr>
<td>((\text{NaCl})<em>{0.3}(\text{NaBr})</em>{0.5}(\text{NaI})_{0.2})</td>
<td>2.990 (3.6714)</td>
<td>1.633 (1.7745)</td>
<td>((\text{NaCl})<em>{0.266}(\text{NaBr})</em>{0.599}(\text{NaI})_{0.135})</td>
</tr>
<tr>
<td>((\text{NaCl})<em>{0.5}(\text{NaBr})</em>{0.3}(\text{NaI})_{0.2})</td>
<td>2.775 (3.6714)</td>
<td>1.615 (1.7745)</td>
<td>((\text{NaCl})<em>{0.489}(\text{NaBr})</em>{0.367}(\text{NaI})_{0.144})</td>
</tr>
<tr>
<td>((\text{NaCl})<em>{0.7}(\text{NaBr})</em>{0.1}(\text{NaI})_{0.2})</td>
<td>2.566 (3.6714)</td>
<td>1.598 (1.7745)</td>
<td>((\text{NaCl})<em>{0.693}(\text{NaBr})</em>{0.129}(\text{NaI})_{0.178})</td>
</tr>
<tr>
<td>((\text{NaCl})<em>{0.1}(\text{NaBr})</em>{0.5}(\text{NaI})_{0.4})</td>
<td>3.285 (3.6714)</td>
<td>1.683 (1.7745)</td>
<td>((\text{NaCl})<em>{0.096}(\text{NaBr})</em>{0.534}(\text{NaI})_{0.376})</td>
</tr>
<tr>
<td>((\text{NaCl})<em>{0.3}(\text{NaBr})</em>{0.3}(\text{NaI})_{0.4})</td>
<td>2.986 (3.6714)</td>
<td>1.647 (1.7745)</td>
<td>((\text{NaCl})<em>{0.336}(\text{NaBr})</em>{0.378}(\text{NaI})_{0.286})</td>
</tr>
<tr>
<td>((\text{NaCl})<em>{0.5}(\text{NaBr})</em>{0.1}(\text{NaI})_{0.4})</td>
<td>2.858 (3.6714)</td>
<td>1.645 (1.7745)</td>
<td>((\text{NaCl})<em>{0.510}(\text{NaBr})</em>{0.091}(\text{NaI})_{0.399})</td>
</tr>
</tbody>
</table>
Figure 6: Composition dependence of density (d) for (NaCl)$_x$(NaBr)$_{1-x}$(NaI)$_{1-y}$ crystals.
Figure 7: Composition dependence of refractive index for \((\text{NaCl})_x(\text{NaBr})_{-x}(\text{NaI})_{1-y}\) crystals