CHAPTER -II

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 composition of all the crystals grown. In addition, the results obtained from these experiments are reported and discussed.

2.1. Importance

Growth of single crystals ranges from a small inexpensive technique to complex sophisticated process and crystallization time ranges from minutes, hours, days and to months. Crystal growth 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 growth to occur equilibrium must be disturbed by a change of the correct sign in temperature, pressure, chemical potential (e.g. saturation), electro chemical 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 growth.

Crystal growth 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.

2.2. Formation of crystals

Three main categories of crystal growth methods are

Growth from the solid: S→S processes involving solid-solid phase transition

Growth from the melt: L→S processes involving Liquid-Solid phase transition

Growth from Vapour: V→S processes involving Vapour-solid phase transition

We have four main categories of crystal growth techniques.

Solid growth, vapour growth, melt growth and solution growth.

The following shows how these main categories break down into subfamilies of related growth techniques.

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Crystal growth

(i) From melt          (ii) From solid          (iii) From Vapour      (iv) From solution

(i) From melt

With crucibles  (Bridgeman and Stockbarger)

Without Crucibles  (Kyropoulis and Czochrakki)
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A brief description of the slow evaporation technique for growing single crystals is given in this chapter.

2.3. Low temperature solution growth

Growth of crystals from aqueous solution is one of the ancient methods of crystal growth. The method of crystal growth from low temperature aqueous solutions is extremely popular in the production of many technologically important crystals. The growth of the crystals by low temperature solution growth involves weeks, months and sometimes years. Materials having moderate to high solubility in temperature range, ambient to 100°C at atmospheric pressure can be grown by low-temperature solution method. The low temperature solution growth is well suited to those materials
which suffer from decomposition in the melt or in the solid at high temperatures and which undergo structural transformations while cooling from the melting point.

The low temperature solution growth technique also allows variety of different morphologies and polymorphic forms of the same substance can be grown by variations of growth conditions or of solvent. The proximity to ambient temperature reduces the possibility of major thermal shock to the crystal both during growth and on removal from the apparatus.

The main disadvantages of the low temperature solution growth are the slow growth rate in many cases and the ease of solvent inclusion into the growing crystal. Under the controlled conditions of growth the solvent inclusion can be minimized and the high quality of the grown crystal can compensate the disadvantage of much longer growth periods. Among the various methods of growing single crystals, solution growth at low temperatures occupies a prominent place owing to its versality and simplicity.

2.3.1. Solution, Solubility and Super solubility

A solution is a homogenous mixture of a solute in a solvent. Solute is the component, which is present in a smaller quantity and that one which gets dissolved in the solution. A solvent of choice is the one with

(i) A good solubility for the given solute.
(ii) A good temperature coefficient of solute solubility.
(iii) Less viscosity
(iv) Less corrosion and non-toxicity
(v) Small vapour pressure
(vi) Cost advantage

It is known that the choice of solvent provides some control over crystal habit and this effect depends on the interaction of the surface of the crystal as it grows and the solvent molecules. Sometimes this is sufficient to result in the precipitation of a new crystalline phase. Also this effect is related to the influence of impurities or additives upon habit. Commonly used solvents are water (both light and heavy), ethanol, methanol, acetone, carbon tetrachloride, hexane, xylene and many others. Almost 90% of the crystals produced from low-temperature solutions are grown by using water as a solvent.

Solubility of the material in a solvent decides the amount of the material, which is available for the growth and hence defines the total size limit. If the solubility is too high, it is difficult to grow bulk single crystals and too small a solubility restricts the size and growth rate of the crystals. Solubility gradient is another important parameter, which dictates the growth procedure.

Super saturation is an important parameter for the solution growth process. The crystal grows by the accession of the solute in the solution as a degree of super saturation is maintained. The solubility data at various temperatures are essential to determine the level of super saturation. Hence the solubility of the solute in the chosen solvent must be determined before starting the growth process.

In order to grow crystals, the solution must be super saturated; the concentration of the solution is more than the equilibrium concentration. The degree of super saturation of a solution is defined using the concept of absolute super saturation.
Low temperature solution growth can be subdivided into the following methods.

i. Slow cooling method

ii. Slow evaporation method

iii. Temperature gradient method

2.3.2. Crystallization by solvent evaporation

In this method, an excess of a given solute is established by utilizing the difference between the rates of evaporation of the solvent and the solute. In the solvent evaporation method, the solution loses particles, which are weakly bound to other components, and therefore, the volume of the solution decreases. In almost all cases, the vapour pressure of the solvent above the solution is higher than the vapour pressure of the solute and, therefore the solvent evaporates more rapidly and the solution becomes supersaturated. Usually, it is sufficient to allow the vapour formed above the solution to escape freely into the atmosphere. Typical growth conditions involve temperature stabilization to about ±0.005°C and rates of evaporation of few mm³/hr.

2.4. Growth of sample crystals of NaₙK₁₋ₓCl

All the alkali halides are soluble in water except NaF and LiF and in principle they can be crystallized from solution. Small sized single crystals can be grown from aqueous solution with or without the addition of impurities. Since all the alkali halides have concurrent melting points usually they are grown from the melt. But Mahadevan and his coworkers [38, 40, 42, 45, 92, 93] found that the transparency of the crystals is reduced, when the crystals are cooled from high temperature to the room temperature due
to the introduction of thermal defects. So, in order to grow transparent crystals of alkali halides low temperature solution growth method is preferred in the present study regardless of their size.

2.4.1. Determination of saturated concentration

The saturated concentration of NaCl solution in molar units may be determined as follows.

Take 10gm of synthesized NaCl in a beaker and add initially 5cc of double distilled water. Stir with a glass rod and keep the experimental temperature constant here is at 30°C. Add drop by drop of distilled water till the solute completely dissolves at that temperature. Now measure the volume of the solution thus prepared the following formula, \( X_0 \) can be found out.

\[
X_0 = m_0 \times \frac{1000}{M} \times V_0
\]

Where \( m_0 = \) Amount of solute (NaCl) (10 gm)

\( M = \) Molecular weight of NaCl

\( V_0 = \) Volume of the solution prepared and measured.

In a similar way saturated concentration of KCl solution in molar units may also be determined.
2.4.2. Preparation of super saturated solution

The amount of sodium chloride \((m_1)\) and amount of Potassium Chloride \((m_2)\) in grams for preparing the required amount of super saturated solution of \(\text{Na}_x \text{K}_{1-x} \text{Cl}\) may be obtained by using the formulae.

\[
m_1 = \left(\frac{M_1 x V x S}{1000}\right) x \text{ in gram units}
\]

\[
m_2 = \left(\frac{M_2 x V x S}{1000}\right) (1 - x) \text{ in gram units}
\]

Where \(M_1\) is the molecular weight of \(\text{NaCl}\), \(M_2\) is the molecular weight of \(\text{KCl}\), \(S\) is the supersaturated concentration in molar units (in our case) and \(V\) is the required volume of the solution \((V = 40 \text{ ml in our experiment})\) and \(x\) is the composition of \(\text{NaCl}\).

The aqueous solution for a particular supersaturated concentration of the substance was prepared by dissolving the required amount of \(\text{NaCl}\) \((m_1)\) and \(\text{KCl}\) \((m_2)\) mixture in slightly insufficient volume of solvent at a temperature slightly higher than experimental temperature. Then the solution was transferred to a measuring jar and the volume is made \(V\) ml by adding the required amount of solvent. Super saturation was achieved by cooling the solution naturally to the experimental temperature 32°C.

2.4.3. Growth of mixed crystals of \(\text{Na}_x \text{K}_{1-x} \text{Cl}\)

\(\text{AnalaR grade NaCl and KCl substances were taken supersaturated solution of Na}_x \text{K}_{1-x} \text{Cl for various values of } x(x = 0.2, 0.4, 0.5, 0.6, 0.8)\) were prepared as described above in identical conditions. Totally 7 solutions (5 mixed and 2 end members) were
prepared and taken in the beakers. They were kept in a undisturbed place. The beakers were closed with the help of a paper and holes were put on the paper for evaporation. After three weeks, tiny crystals were formed and were harvested after 5 weeks.

2.4.4. Growth of ZnS added mixed Na\textsubscript{x} K\textsubscript{1-x} Cl crystals

ZnS salt is non-soluble in water, so 1 normal solution of ZnS was prepared from dissolving it in dilute nitric acid and this solution is used for the addition of impurity. Few drops of ammonium hydroxide solution was added to maintain the PH value equal to 6.

20 ml of the super saturated solution, thus prepared for the undoped pure and mixed crystals were taken in beakers. Totally 7 solutions were taken. 5 ml of the prepared ZnS solution were added to each 20 ml of supersaturated solutions. They were also kept in the undisturbed place and grown crystals were harvested after 5 weeks.

2.5. Quantitative Composition analysis

2.5.1. Energy Dispersive Analysis of X-rays

EDAX is a useful technique for confirming the chemical composition as well as the chemical homogeneity present in these samples. All the measurements were carried out, in the present study, using FEI Quanta FEG 200 model scanning electron microscope on large as well as small analysis areas in order to obtain the global composition and the compositions at small regions at various parts of the sample. In this technique, finely focused electron beam strikes the surface of a conducting sample or a poorly conducting sample made conducting by gold - coating surface. The energy of the electron beam is
typically in the range of 10-20 Kev.

As the electron beam is scanned across the sample surface, it generates X-ray fluorescence (the principle is illustrated in Figure 2.) from the atoms in its path, i.e. from the specific part of the sample where electron beam strikes it. The energy of each X-ray photon is characteristic of the element which produces it. The X-rays are generated in a region about 2 microns in depth and thus EDAX is not a surface sensitive technique. The compositions obtained from these measurements are same as expected from their chemical composition ratio within the error limit of ±5% or better. The sample is mounted in the SEM chamber and the system is evacuated to \(10^{-6}\) torr. The electron beam is scanned over selected areas according to the requirements. The observed microstructure is captured at appropriate magnification as video image picture frames at a CRT or stored into a computer.

2.5.2. EDAX Experimental set up

Apart from giving the high resolution surface morphological images, the quanta 200 FEG also has the analytical capabilities such as detecting the presence of elements down to Boron (B) on any solid conducting materials through the energy dispersive X-ray spectrometry (EDX) providing crystalline information from the few nanometer depth of the material surface via electron back scattered detection (BSD) system attached with microscope and advanced technological PBS (WDS) for elemental analysis. It has a resolution of 1.2 nm gold particle separation on a carbon substrate and the magnification power of about minimum 12 x to greater than \(10^5\) x.
Fig.2. SEM EDX Apparatus
2.5.3. Scanning electron microscopy

The scanning electron microscope (SEM) uses a focused beam of high-energy electrons to generate a variety of signals at the surface of solid specimens [94]. The signals that derive from electron sample interactions reveal information about the sample including external morphology (texture), chemical compositions and crystalline structure and orientation of materials making up the sample. In most applications, data are collected over a selected area of the surface of the sample and a two-dimensional image is generated that displays spatial variations in these properties. Areas ranging from approximately 1 cm to 5 microns in width can be imaged in a scanning mode using conventional SEM techniques (magnification ranging from 20X to approximately 30,000X, spatial resolution of 50 to 100 nm). The SEM is also capable of performing analysis of selected point locations on the sample; this approach is especially useful in quantitatively or semi-qualitatively determining chemical compositions (using EDS), crystalline structure and crystal orientations (using EBSD). The design and function of the SEM is very similar to the EPMA and considerable overlap in capabilities exists between the two instruments.

Accelerated electrons in a SEM carry significant amount of kinetic energy and this energy is dissipated as a variety of signals produced by electron-sample interactions when the incident electrons are decelerated in the solid sample. These signals include secondary electrons (that produce SEM images), back scattered electrons (BSE), diffracted back scattered electrons (EBSD) that are used to determine crystal structures and orientations of minerals), photons (characteristic X-rays that are used for elemental analysis and continuum X-rays), visible light (Cathodoluminescence-CL), and heat.
Secondary electrons and back scattered electrons are commonly used for imaging samples. Secondary electron are most valuable for illustrating contrasts in composition in multiphase samples (i.e. for rapid phase discrimination). X-ray generation is produced by inelastic collisions of the incident electrons with electrons in discrete orbitals (shells) of atoms in the sample. As the excited electrons return to lower energy states, that yield X-rays that are of a fixed wave length (that is related to the difference in energy levels of electrons in different shells for a given element). Thus, characteristic X-rays are produced for each element in a mineral that is “excited” by the electron beam. SEM analysis is considered to be “non-destructive; that is, X-rays generated by electron interactions do not lead to volume loss of the sample, so it is possible to analyze the same materials repeatedly.

2.6. Results obtained

2.6.1. Grown Crystals

In the present study fourteen crystals (five mixed crystals viz. Na\textsubscript{x} K\textsubscript{1-x} Cl, \(x = 0.2, 0.4, 0.5, 0.6 \& 0.8\), ZnS doped Na\textsubscript{x} K\textsubscript{1-x} Cl \(x = 0.2, 0.4, 0.5, 0.6\) and \(0.8\), two end member crystals (NaCl and KCl) and ZnS added two end member crystals) were grown from the aqueous solution by slow evaporation technique under identical conditions. The end member crystals were grown for comparison purposes. The photographs of pure and ZnS doped crystals are shown in Figures 3, 4 respectively. They are found to be transparent and stable. The mixed and doped crystals grown in the present study are found to be harder than the end member crystals except a few, it is confirmed by the microhardness measurement (Ref.Chapter IV). The average size of the crystals obtained in the present study is about \(6 \times 6 \times 2\) mm and the maximum size of the crystal obtained
in the present study is 8 x 7 x 3 mm. The dopant addition has no influence on the size of the crystal.

Fig.3. Undoped Na\textsubscript{x}K\textsubscript{1-x}Cl Crystals

Fig.4. ZnS doped Na\textsubscript{x}K\textsubscript{1-x}Cl Crystals
2.6.2. Composition

The weight percentage, the estimated composition and the mole percentage of the dopant ZnS for doped crystals are provided in Table 7 along with the actual composition taken. The EDAX spectrum of all the mixed and ZnS added mixed crystals are given in Figures 5-16. The compositions calculated from the weight percentage for all the mixed crystals are provided in Table 7 It is found that the estimated composition of the pure and ZnS doped mixed crystals agreed well with the actual composition taken.
Fig. 5. EDAX spectrum of undoped Na$_{0.2}$K$_{0.8}$Cl crystal

Fig. 6. EDAX spectrum of undoped Na$_{0.4}$K$_{0.6}$Cl crystal

Fig. 7. EDAX spectrum of undoped Na$_{0.5}$K$_{0.5}$Cl crystal

Fig. 8. EDAX spectrum of undoped Na$_{0.6}$K$_{0.4}$Cl crystal

Fig. 9. EDAX spectrum of undoped Na$_{0.8}$K$_{0.2}$Cl crystal
Fig. 10. EDAX spectrum of ZnS doped Na$_{0.2}$K$_{0.8}$Cl crystal

Fig. 11. EDAX spectrum of ZnS doped Na$_{0.4}$K$_{0.6}$Cl crystal

Fig. 12. EDAX spectrum of ZnS doped Na$_{0.5}$K$_{0.5}$Cl crystal

Fig. 13. EDAX spectrum of ZnS doped Na$_{0.6}$K$_{0.4}$Cl crystal

Fig. 14. EDAX spectrum of ZnS doped Na$_{0.8}$K$_{0.2}$Cl crystal
Fig. 15. EDAX spectrum of ZnS doped NaCl crystal

Fig. 16. EDAX spectrum of ZnS doped KCl crystal
Table 7. Weight percentage and estimated composition values together with the composition taken for pure and ZnS doped crystals.

<table>
<thead>
<tr>
<th>System</th>
<th>Weight Percentage of</th>
<th>Estimated composition</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Na</td>
<td>K</td>
</tr>
<tr>
<td>Undoped mixed crystals</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NaCl</td>
<td>14.95</td>
<td>00.02</td>
</tr>
<tr>
<td>KCl</td>
<td>35.38</td>
<td>00.54</td>
</tr>
<tr>
<td>Na0.2 K0.8 Cl</td>
<td>01.46</td>
<td>44.25</td>
</tr>
<tr>
<td>Na0.4 K0.6 Cl</td>
<td>02.15</td>
<td>45.64</td>
</tr>
<tr>
<td>Na0.5 K0.5 Cl</td>
<td>04.75</td>
<td>42.81</td>
</tr>
<tr>
<td>Na0.6 K0.4 Cl</td>
<td>20.08</td>
<td>22.29</td>
</tr>
<tr>
<td>Na0.8 K0.2 Cl</td>
<td>39.98</td>
<td>00.28</td>
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<tr>
<td>ZnS doped mixed crystals</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NaCl</td>
<td>37.77</td>
<td>-</td>
</tr>
<tr>
<td>KCl</td>
<td>-</td>
<td>15.11</td>
</tr>
<tr>
<td>Na0.2 K0.8 Cl</td>
<td>01.89</td>
<td>13.74</td>
</tr>
<tr>
<td>Na0.4 K0.6 Cl</td>
<td>04.15</td>
<td>14.28</td>
</tr>
<tr>
<td>Na0.5 K0.5 Cl</td>
<td>01.16</td>
<td>13.97</td>
</tr>
<tr>
<td>Na0.6 K0.4 Cl</td>
<td>24.62</td>
<td>27.63</td>
</tr>
<tr>
<td>Na0.8 K0.2 Cl</td>
<td>02.38</td>
<td>14.76</td>
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2.6.3. Grain Size

Morphological characterization of the crystals was performed by using scanning electron microscopy (SEM). The SEM photographs of all the grown crystals are shown in Figures 17-30.

The square shaped clusters were formed and the changes in SEM images observed for the mixed crystals with those end members indicate that they are mixed crystals. Except ZnS doped Na$_{0.2}$ K$_{0.8}$ Cl crystal, all are in micro meter scale. But in the case of ZnS doped Na$_{0.2}$ K$_{0.8}$ Cl crystal the size of the cluster decreased to nano meter scale (931.4 nm). The maximum and minimum size of the clusters are provided in Table 8. This indicates that the size of the crystallites in the case of ZnS added alkali halide crystals grown in the present study are very small leading to become nano crystalline phases. Particularly, in the case of ZnS added Na$_{0.2}$ K$_{0.8}$ Cl, Pretty Well indicates that the system prepared is a nano composite. When the NaCl concentration increases the grain size gets increased and compared to undoped mixed crystals the grain sizes of the cluster increased in the doped mixed crystals.

Mijangos and his co-workers [47] found that the alkali halide mixed crystals form a platform for the preparation of nano composites. The grain size found in the present study is in line with this.
Table 8. Values of grain size (μm) for undoped and ZnS doped Na$_x$ K$_{1-x}$ Cl crystals.

<table>
<thead>
<tr>
<th>System</th>
<th>Grain Size (μm)</th>
<th></th>
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</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Undoped</td>
<td>ZnS Doped</td>
</tr>
<tr>
<td></td>
<td>Max.</td>
<td>Min.</td>
<td>Max.</td>
</tr>
<tr>
<td>NaCl</td>
<td>8.57</td>
<td>2.56</td>
<td>9.06</td>
</tr>
<tr>
<td>KCl</td>
<td>14.09</td>
<td>9.23</td>
<td>22.80</td>
</tr>
<tr>
<td>Na$<em>{0.2}$ K$</em>{0.8}$Cl</td>
<td>6.28</td>
<td>3.30</td>
<td>17.92</td>
</tr>
<tr>
<td>Na$<em>{0.4}$ K$</em>{0.6}$Cl</td>
<td>3.75</td>
<td>2.48</td>
<td>11.18</td>
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<tr>
<td>Na$<em>{0.5}$ K$</em>{0.5}$Cl</td>
<td>10.75</td>
<td>5.07</td>
<td>37.99</td>
</tr>
<tr>
<td>Na$<em>{0.6}$ K$</em>{0.4}$Cl</td>
<td>7.03</td>
<td>2.88</td>
<td>34.63</td>
</tr>
<tr>
<td>Na$<em>{0.8}$ K$</em>{0.2}$Cl</td>
<td>5.47</td>
<td>3.13</td>
<td>7.82</td>
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</table>
Fig. 17. SEM image of undoped NaCl crystal

Fig. 18. SEM image of undoped KCl crystal

Fig. 19. SEM image of ZnS doped NaCl crystal

Fig. 20. SEM image of ZnS doped KCl crystal
Fig. 21. SEM image of undoped Na$_{0.2}$K$_{0.8}$Cl crystal

Fig. 22. SEM image of undoped Na$_{0.4}$K$_{0.6}$Cl crystal

Fig. 23. SEM image of undoped Na$_{0.5}$K$_{0.5}$Cl crystal

Fig. 24. SEM image of undoped Na$_{0.6}$K$_{0.4}$Cl crystal

Fig. 25. SEM image of undoped Na$_{0.8}$K$_{0.2}$Cl crystal
Fig. 26. SEM image of ZnS doped Na<sub>0.2</sub>K<sub>0.8</sub>Cl crystal

Fig. 27. SEM image of ZnS doped Na<sub>0.4</sub>K<sub>0.6</sub>Cl crystal

Fig. 28. SEM image of ZnS doped Na<sub>0.5</sub>K<sub>0.5</sub>Cl crystal

Fig. 29. SEM image of ZnS doped Na<sub>0.6</sub>K<sub>0.4</sub>Cl crystal

Fig. 30. SEM image of ZnS doped Na<sub>0.8</sub>K<sub>0.2</sub>Cl crystal