CHAPTER - II

GROWTH PROCEDURE

The growth procedures of the undoped and doped mixed crystals are provided in this chapter. The observed composition dependence and grain sizes of all the sixteen crystals are reported and discussed in this chapter.

2.1. Growth of sample crystals NaCl\textsubscript{x}Br\textsubscript{1-x}

All the alkali halides except LiF and NaF are soluble in water and can be crystallised from solution, but only small size crystals can be grown from the aqueous solution with or without addition of impurities. Since all the alkali halides have congruent melting points they are usually grown from melt. Mahadevan and his co-workers [112,164-166, 180] have found that the transparency of the crystal were reduced and become white when the crystals were cooled from high temperature to the room temperature, so in order to grow transparent single crystals of mixed alkali halides, we gone for slow evaporation technique regardless of the size.

Also Mijangose and his co-workers [181] have found that alkali halides form a best platform to produce nano-composites. In this view we added ZnS as dopant. In the present study, undoped and ZnS doped mixed crystals of NaCl\textsubscript{x}Br\textsubscript{1-x} were grown from the aqueous solution by taking different values of x viz 0.4, 0.5, 0.6, 0.7, 0.8, 0.9 along with two end member crystals.
2.1.1. Determination of Saturate concentration

The saturated concentration \( (x_0) \) of NaCl and NaBr solution in molar units may be determined as follows.

Take 10gm of AnalaR grade NaCl salt in a beaker and add initially 5cc of doubly distilled water. Stir with a glass rod and keep the experimental temperature constant here it is 32°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

\[
X_0 = \frac{m_0 x 1000}{MV_0}
\]

where \( m_0 \) = amount of solute taken (NaCl) (10gm)

\( M \) = Molecular weight of NaCl

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

In this present study \( X_0 \) of NaCl is found to be 2.8M

In the similar way, the saturated concentration of NaBr is found to be 7.13M.

2.1.2. Preparation of Supersaturated solution

The amount of sodium chloride \( (m_1) \) and amount of sodium bromide \( (m_2) \) in grams for preparing the required amount of supersaturated solution of \( \text{NaCl}_x\text{Br}_{(1-x)} \) may be obtained by using the formulae

\[
m_1 = \left( \frac{M_2 V_0 S}{1000} \right) x \text{ in gram units}
\]

\[
m_2 = \left( \frac{M_2 V_0 S}{1000} \right) (1 - x) \text{ in gram units}
\]
where $M_1$ and $M_2$ are molecular weight of NaCl and NaBr respectively. $S$ is the supersaturated concentration in molar units, and $V$ is the required volume of the solution ($V = 40$ ml) and $x$ is the composition of NaCl.

The aqueous solution of a particular supersaturated concentration (25ml in the present work) of the substance was prepared by dissolving the required amount of NaCl ($m_1$) and NaBr ($m_2$) 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. Supersaturation was achieved by cooling the solution naturally to the experimental temperature 32°C.

2.1.3. Growth of mixed NaCl$_x$Br$_{(1-x)}$ crystals

AnalaR grade NaCl and NaBr substances were taken. Supersaturated solutions of NaCl$_x$Br$_{(1-x)}$ for various values of $x$ ($x = 0.4, 0.5, 0.6, 0.7, 0.8, 0.9$) were prepared as described above in identical conditions. Totally 8 solutions (6 mixed and 2 end members) were prepared in identical conditions and taken in the beakers. They were kept in a undisturbed place. The beakers were covered 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.

2.1.4. Growth of ZnS added mixed NaCl$_x$Br$_{(1-x)}$ crystals

Preparation of ZnS solution.

ZnS salt is non soluble in water, so 1N solution of ZnS was prepared by dissolving it in dilute nitric acid and is used as the dopant. The PH value of the solution is adjusted by adding sufficient drops of NH$_4$OH solutions.
20 ml of the supersaturated solution, thus prepared for the undoped pure and mixed crystals were taken in beakers. Totally 8 solutions were taken 2.5 ml of the prepared ZnS solution were added to each 25 ml of supersaturated solutions. They were also kept in the undisturbed place and allowed them to grown. Grown crystals were harvested after 5 weeks

2.2. Determination of Composition and Grain

The composition dependence of properties of mixed crystals find an important place, while carrying out the growth and characterisation studies on mixed crystals. So accurate determination of the composition is as important as the determination of the property itself.

2.2.1. Experimental Details

A scanning electron microscope (SEM) images a sample by scanning it with a high-energy beam of electrons in a raster scan pattern. The electrons interact with the atoms of sample producing signals which contain information’s regarding the surface topography, composition, as well as other properties such as electrical conductivity.

The excess energy of the electron that migrates to an inner shell to fill the newly created can do more than emit an X-ray. Often instead of X-ray emission, the excess energy is transferred to a third electron from a further outer shell, promoting its ejection, the outputs of EDAX analysis are EDAX spectra.

The fundamental principles of scanning electron microscope are that, the electron beam is thermionically emitted from an electron gun fitted with a tungsten filament cathode. Tungsten, a low cost metal, is normally used in thermionic electron
guns because it has the high melting point and low vapour pressure, thereby allowing it to be heated for electron emission. Other types of electron emitters include lanthanum hexaboride (LaBr) cathodes, which can be used in a standard tungsten filament SEM if the vacuum system is upgraded and field emission guns (FEG), which may be of cold-cathode type using tungsten single crystal emitters or the thermally assisted Schottky type, using emitters of zirconium oxide. The electron beam, which typically has an energy ranging from 0.5 keV to 40 keV, is focused by one or two condenser lenses to a pot ~ 0.4 nm - 5 nm in diameter.

Electron beam passes through pairs of scanning coils or pairs of deflector plates in the electron column fall in the final lens, which deflect the beam in the x and y axes so that it scans in a raster fashion over a rectangular area of the sample surface.

When the primary electron beam interacts with the sample, the electrons lose energy by repeated random scattering and absorption within a teardrop shaped volume of the specimen, which extends from less than 100 nm to around 5 µm into the surface. The size depends on the electron's landing energy, the atomic number of the specimen and the specimen's density.

The energy exchange between the electron beam and the sample results in the reflection of high energy electrons by elastic scattering, emission of secondary electrons by inelastic scattering and the emission of electromagnetic radiation, each of which can be detected by specialized detectors. The beam current absorbed by the specimen can also be detected and used to create images of the distribution of specimen current. Electronic amplifiers of various types are used to amplify the signals which are displayed as variations in brightness on a cathode ray tube. The raster scanning of the CRT display is synchronized with that of the beam on the
specimen in the microscope, and the resulting image is therefore a distribution map of the intensity of the signal being emitted from the scanned area of the specimen. The image may be captured by photography from a high resolution cathode ray tube. In the modern machines, the image is captured digitally and displayed on a computer monitor as well as saved in the computer's hard disk.

The F E I Quanta FEG 200 scanning electron microscope (SEM) is a versatile high resolution scanning electron microscope with three modes of operation, namely, the high vacuum (HV) mode for metallic (electrically conducting) sample, low vacuum (LV) and environment scanning electron microscope (ESEM) modes for insulating, ceramic, polymeric (electrically insulating) and biological samples respectively. 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 (Edax) providing crystalline information from the few nanometre 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 of 12x to greater than $10^5x$.

In the present study, the SEM image and EDAX spectrum of all the grown crystals were taken by using F E I Quanta FEG 200 model instrument at I.I.T Madras, the photograph of the instrument is shown in the Fig.6.
Fig. 6. Experimental setup Scanning electron Microscope and EDAX
2.3. Results obtained

2.3.1. Growth of mixed crystals

The undoped mixed crystals of NaCl$_x$Br$_{(1-x)}$ are shown in the photograph 7, the ZnS added mixed crystals were shown in photograph 8 and pure and doped end members crystals are shown in photograph 9. All the crystals (two undoped end members, six undoped mixed crystals, two doped end members and six doped mixed crystals) are found to be transparent and good quality crystals. The maximum dimensions obtained are 11x11x6mm for NaCl$_{0.7}$Br$_{0.3}$ crystal. The average dimension of all the grown crystals was 6x6x5mm.
Fig. 7. Photograph of undoped mixed crystals

Fig. 8. Photograph of ZnS doped mixed crystals

Fig. 9. Photograph of Pure and ZnS doped End member crystals
2.3.2. Grain Size

The SEM images for all the sixteen samples are shown in figures 10 to 24. The SEM images show that the sample consist of grains about less 16µm are spread across the matrix in the form of square plate clusters with dimensions in the range of 1µm to 16 µm. The grain size of the entire sample is provided in Table 10. It is found that, the grain size has been reduced in the case of ZnS added mixed system when compared to the undoped mixed crystals. Especially in the cases of undoped NaCl$_{0.9}$Br$_{0.1}$, ZnS added NaCl$_{0.8}$Br$_{0.2}$ and NaCl$_{0.9}$Br$_{0.1}$ samples, the grain sizes have reduced to nanometre scale viz., 170 nm, 344 nm and 431 nm respectively. Mijangas and his co-workers [181] have found that alkali halides form a platform to produce nano-composites. They obtained nano-composites from the melt of KBr, RbCl, RbBr, KI and RbI of 5 to 100 nanometre size. In a similar way nanometre grains are also obtained in the present study.
Fig. 10. SEM image of NaCl crystal

Fig. 11. SEM image of NaBr crystal

Fig. 12. SEM image of ZnS doped NaCl crystal

Fig. 13. SEM image of ZnS doped NaBr crystal
Fig. 14. SEM image of undoped NaCl$_{0.4}$Br$_{0.6}$ crystal.

Fig. 15. SEM image of undoped NaCl$_{0.5}$Br$_{0.5}$ crystal.

Fig. 16. SEM image of undoped NaCl$_{0.6}$Br$_{0.6}$ crystal.

Fig. 17. SEM image of undoped NaCl$_{0.7}$Br$_{0.3}$ crystal.

Fig. 18. SEM image of undoped NaCl$_{0.8}$Br$_{0.2}$ crystal.

Fig. 19. SEM image of undoped NaCl$_{0.9}$Br$_{0.1}$ crystal.
Fig. 20. SEM image of ZnS doped NaCl_{0.4}Br_{0.6} crystal

Fig. 21. SEM image of ZnS doped NaCl_{0.5}Br_{0.5} crystal

Fig. 22. SEM image of ZnS doped NaCl_{0.6}Br_{0.4} crystal

Fig. 23. SEM image of ZnS doped NaCl_{0.7}Br_{0.3} crystal

Fig. 24. SEM image of ZnS doped NaCl_{0.8}Br_{0.2} crystal

Fig. 25. SEM image of ZnS doped NaCl_{0.9}Br_{0.1} crystal
Table 10. Grain size (µm) of all grown crystals.

<table>
<thead>
<tr>
<th>Actual Compositions</th>
<th>Undoped mixed crystals (µm)</th>
<th>ZnS doped mixed crystals (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Max</td>
<td>Mini</td>
</tr>
<tr>
<td>NaCl</td>
<td>2.56</td>
<td>8.57</td>
</tr>
<tr>
<td>NaBr</td>
<td>11.18</td>
<td>8.71</td>
</tr>
<tr>
<td>NaCl&lt;sub&gt;0.4&lt;/sub&gt;NaBr&lt;sub&gt;0.6&lt;/sub&gt;</td>
<td>2.96</td>
<td>2.41</td>
</tr>
<tr>
<td>NaCl&lt;sub&gt;0.5&lt;/sub&gt;NaBr&lt;sub&gt;0.5&lt;/sub&gt;</td>
<td>3.38</td>
<td>11.5</td>
</tr>
<tr>
<td>NaCl&lt;sub&gt;0.6&lt;/sub&gt;NaBr&lt;sub&gt;0.4&lt;/sub&gt;</td>
<td>14.95</td>
<td>9.19</td>
</tr>
<tr>
<td>NaCl&lt;sub&gt;0.7&lt;/sub&gt;NaBr&lt;sub&gt;0.3&lt;/sub&gt;</td>
<td>1.32</td>
<td>2.28</td>
</tr>
<tr>
<td>NaCl&lt;sub&gt;0.8&lt;/sub&gt;NaBr&lt;sub&gt;0.2&lt;/sub&gt;</td>
<td>0.873</td>
<td>0.769</td>
</tr>
<tr>
<td>NaCl&lt;sub&gt;0.9&lt;/sub&gt;NaBr&lt;sub&gt;0.1&lt;/sub&gt;</td>
<td>0.431</td>
<td>0.529</td>
</tr>
</tbody>
</table>
2.3.3. Composition determination from EDAX

EDAX Spectra recorded for all sixteen grown crystals are shown in figures 26 to 41. EDAX spectrum displaces peaks corresponding to energy level for which the most X-rays had been received. Each of these peaks is unique to an atom and therefore corresponds to single element Na, Cl, Br, Zn and S. From figs the energy peaks at 1 Kev, 2.175 Kev and 1.5 Kev are characteristic peaks of Sodium, Chlorine & Bromine respectively. In the case of ZnS added system, Zn and S peaks are appeared at 8.9 Kev and 2.4 Kev respectively. But in the case of ZnS doped NaCl system, the Zn Peak appeared at 1 Kev in L Shell.

The EDAX spectra of the ZnS doped system reveal that the dopant atoms Zn$^{2+}$ and S$^{2-}$ added is clearly incorporated with the host matrix. Higher the peak in a spectrum, the more concentration of the element in the specimen and EDAX spectrum not only identifies the element corresponding to each of its peak, but type of X-ray to it corresponds as well. A peak corresponding to the amount of energy possessed by X-rays emitted by an electron L-Shell going down to K-shell is identified as a K$_{\alpha}$ peak. The peak corresponding to X-ray emitted by M-shell electron going to the K-shell is identified as a K$_{\beta}$ peaks. It is confirmed that all the elements are mostly present in K-shell but the Bromine atoms in the undoped mixed crystals are present in L-shell. The weight percentage of all the atoms present in mixed and doped mixed systems are provided along with the composition of the starting material in Table.11. The EDAX spectrum can also be used to estimate the bulk composition of the grown crystals from the weight percentage. The estimated composition of the grown crystals is also provided in Table.11. It is found that the estimated composition of the material taken is well agreed with the actual composition of the sample.
Fig. 26. EDAX spectrum of NaCl crystal

Fig. 27. EDAX spectrum of NaBr crystal

Fig. 28. EDAX spectrum of ZnS NaCl crystal

Fig. 29. EDAX spectrum of ZnS doped NaBr crystal
Fig. 30 EDAX spectrum of undoped NaCl$_{0.4}$Br$_{0.6}$ crystal

Fig. 31 EDAX spectrum of undoped NaCl$_{0.5}$Br$_{0.5}$ crystal

Fig. 32 EDAX spectrum of undoped NaCl$_{0.6}$Br$_{0.4}$ crystal

Fig. 33 EDAX spectrum of undoped NaCl$_{0.7}$Br$_{0.3}$ crystal

Fig. 34 EDAX spectrum of undoped NaCl$_{0.8}$Br$_{0.2}$ crystal

Fig. 35 EDAX spectrum of undoped NaCl$_{0.9}$Br$_{0.1}$ crystal
Fig. 36. EDAX spectrum of Zns doped
NaCl0.8Br0.2 crystal

Fig. 37. EDAX spectrum of ZnS doped
NaCl0.9Br0.1 crystal

Fig. 38. EDAX spectrum of Zns doped
NaCl0.6Br0.4 crystal

Fig. 39. EDAX spectrum of ZnS doped
NaCl0.7Br0.3 crystal

Fig. 40. EDAX spectrum of ZnS doped
NaCl0.8Br0.2 crystal

Fig. 41. EDAX spectrum of ZnS doped
NaCl0.9Br0.1 crystal
Table 11. Weight percentage and the estimated compositions of undoped and doped mixed crystals.

<table>
<thead>
<tr>
<th>Actual Compositions</th>
<th>Weight Percentage undoped mixed crystals</th>
<th>Estimated composition of undoped mixed crystals</th>
<th>Weight Percentage doped mixed crystals</th>
<th>Estimated Composition of doped mixed crystals</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Na</td>
<td>Cl</td>
<td>Br</td>
<td>Na</td>
</tr>
<tr>
<td>NaCl$<em>{0.4}$Br$</em>{0.6}$</td>
<td>38.99</td>
<td>20.64</td>
<td>40.47</td>
<td>NaCl$<em>{0.45}$Br$</em>{0.54}$</td>
</tr>
<tr>
<td>NaCl$<em>{0.5}$Br$</em>{0.5}$</td>
<td>38.99</td>
<td>29.45</td>
<td>32.08</td>
<td>NaCl$<em>{0.57}$Br$</em>{0.427}$</td>
</tr>
<tr>
<td>NaCl$<em>{0.6}$Br$</em>{0.4}$</td>
<td>24.66</td>
<td>38.24</td>
<td>37.1</td>
<td>NaCl$<em>{0.64}$Br$</em>{0.346}$</td>
</tr>
<tr>
<td>NaCl$<em>{0.7}$Br$</em>{0.3}$</td>
<td>32.75</td>
<td>42.6</td>
<td>24.65</td>
<td>NaCl$<em>{0.74}$Br$</em>{0.285}$</td>
</tr>
<tr>
<td>NaCl$<em>{0.8}$Br$</em>{0.2}$</td>
<td>36.02</td>
<td>50.69</td>
<td>13.29</td>
<td>NaCl$<em>{0.83}$Br$</em>{0.179}$</td>
</tr>
<tr>
<td>NaCl$<em>{0.9}$Br$</em>{0.1}$</td>
<td>38.37</td>
<td>52.34</td>
<td>9.29</td>
<td>NaCl$<em>{0.913}$Br$</em>{0.09}$</td>
</tr>
</tbody>
</table>