CHAPTER III

CRYSTAL GROWTH AND MORPHOLOGY OF PURE AND DOPED TRIGLYCINE SULPHATE CRYSTALS
3.1 INTRODUCTION

Triglycine sulphate, \( \text{NH}_2\text{CH}_2(\text{COOH})_3\cdot\text{H}_2\text{SO}_4 \), (TGS) crystal has attracted several researchers not only because of its applications in pure and applied science but also because of its low cost production, easy to grow bulk crystals and water solubility. The major objective of the present work is to modify the triglycine sulphate crystals with suitable dopants to achieve better pyroelectric properties, improved infrared detectivities and higher Curie transition temperature compared to the undoped TGS crystals. Towards these objectives, divalent and trivalent metal ions were used as dopants.

3.2 SYNTHESIS AND CRYSTAL GROWTH

Single crystals of TGS were grown in the ferroelectric phase from the saturated solutions by the slow cooling technique. The triglycine sulphate was prepared by mixing glycine and sulphuric acid in the ratio 3:1 in a double distilled water. The mixture was allowed to stand for 3 days at the temperature of 35°C and then gradually solution was evaporated the solution at 40°C to obtain TGS crystals. Thus obtained crystals were recrystallized thrice from the double distilled water before attempting for bulk single crystal growth. The following reaction was employed to synthesize TGS

\[
3(\text{NH}_2\text{CH}_2\text{COOH}) + \text{H}_2\text{SO}_4 \rightarrow (\text{NH}_2\text{CH}_2\text{COOH})_3 \cdot \text{H}_2\text{SO}_4
\]

The solubility of the TGS in double distilled was determined as a function of temperature. A simple procedure was followed to determine the solubility at one temperature and the procedure was repeated at different temperatures above room temperature to obtained solubility curve of TGS. 100 ml of double distilled water
was taken in a 250 ml conical flask; a known amount of TGS is added stepwise while stirring the solution. The addition of TGS was continued until the dissolution ceases. The procedure was repeated to check the reproducibility. Similarly the solubility of TGS in double distilled water above the room temperatures was also determined. The variation of solubility of TGS in double distilled water as a function of temperature is shown in Figure 3.1. The solubility of TGS varies linearly as the temperature increases. Therefore cooling from elevated temperature or solution evaporation at constant temperature may be adopted to grow single crystals of doped and pure TGS. In the case of the TGS single crystal growth by cooling, the saturation at required temperature was prepared according to the solubility graph.

![Solubility graph](image)

Figure 3.1 : Solubility graph

To obtain larger crystal, the same solution was prepared by dissolving 75.07 gm of glycine in distilled water and mixing 17.77 ml of sulphuric acid. The as grown good quality TGS crystal seed was suspended using nylon thread in the mother solution taken in a growth apparatus. As days progressed the dimensions of the seed crystals increased. Crystals reached their maximum size in a period of one month. TGS crystals were harvested from the growth apparatus after reaching their maximum size. The size of the pure TGS crystal thus obtained is 25 mm × 20 mm × 18 mm.
3.2.1 Preparation of Doped TGS Crystals

Dopants were introduced to the pure TGS crystal during growth by mixing TGS solution with different dopant salt solutions. In the present investigation inorganic dopants Ba$^{2+}$, Cu$^{2+}$, Pb$^{2+}$, Fe$^{3+}$ and Mn$^{2+}$ were used. Solutions of different dopants were prepared using double distilled water and filtered. This is mixed with pure TGS solution. Mixed solution was heated, filtered and poured into a petridish and kept for slow evaporation under ambient condition. Due to slow evaporation of the solvent, supersaturation was achieved and seed crystals were formed in the experimental vessels. A good quality seed crystal was taken and suspended in the mother solution containing suitable quantity of TGS and dopant solution. This procedure was also performed to grow TGS crystals with other dopants. The suspended seed crystal was allowed to grow in the growth apparatus for a period of 30 days, during which the crystal reached its maximum size and then harvested. Table 3.1 gives the summary of the procedure used to obtain doped TGS crystals.

**Table 3.1 : Summary of doped crystal growth**

<table>
<thead>
<tr>
<th>Dopant</th>
<th>Valance of the dopant</th>
<th>Salt used</th>
<th>Amount dissolved in 10.777 gms of TGS</th>
<th>Crystal obtained</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ba</td>
<td>Divalent</td>
<td>Barium chloride</td>
<td>0.081430 gm</td>
<td>BaTGS</td>
</tr>
<tr>
<td>Cu</td>
<td>Divalent</td>
<td>Copper sulphate</td>
<td>0.083230 gm</td>
<td>CuTGS</td>
</tr>
<tr>
<td>Pb</td>
<td>Divalent</td>
<td>Lead nitrate</td>
<td>0.110338 gm</td>
<td>PbTGS</td>
</tr>
<tr>
<td>Fe</td>
<td>Trivalent</td>
<td>Ferric chloride</td>
<td>0.05407 gm</td>
<td>FeTGS</td>
</tr>
<tr>
<td>Mn</td>
<td>Trivalent</td>
<td>Manganous sulphate</td>
<td>0.056336 gm</td>
<td>MnTGS</td>
</tr>
</tbody>
</table>
The maximum size of the doped crystals obtained is 13mm x 12mm x 7mm. Investigations on the optimization of the growth conditions of single crystals containing molecular glycine groups were found to be dependent on the pH-value of the solution. The optimal pH-value for triglycine sulphate growing was found to be 1.5. It has been found that the pH of the solution at the time of crystallization is an important parameter determining the crystallization of the different glycine-sulphate compounds. It has been reported that for the crystallization of TGS crystal the required pH should be ≥ 1.5 [1]. In the present work, the pH of the solution for the crystallization of TGS was at 2.5. The crystal morphology of doped TGS gets slightly modified along a- and b-axis when compared to pure TGS due to the incorporation of the dopants in the crystal lattice. Figure 3.2 depicts the crystal growth apparatus and figure 3.3 (a) – (f) shows the pure and doped TGS crystals grown.

Figure 3.2 : crystal growth apparatus
Figure 3.3 (a) : Pure TGS

Figure 3.3 (b) : TGS doped with Ba$^{2+}$

Figure 3.3 (c) : TGS doped with Cu$^{2+}$

Figure 3.3 (d) : TGS doped with Pb$^{2+}$

Figure 3.3 (e) : TGS doped with Fe$^{3+}$

Figure 3.3 (f) : TGS doped with Mn$^{3+}$
3.3 CRYSTAL MORPHOLOGY

Impurities can have great effect on crystal growth kinetics of the crystals. Morphology of many crystals results from the different growth of various faces, which changes gradually when the dopant is introduced in the mother solution [2]. The characteristic form of pure TGS gets disturbed due to the influence of macromolecules in the solution. Increase in the concentration of the dopants in the TGS solution reduced the size of the (0 1 0) faces and also number of developed faces compared to pure TGS. Figures 3.4(a) - 3.4(f) show the morphology of the crystals grown.

From the modification in morphology of TGS crystals, it may be presumed that the surface diffusion enhanced in the doped TGS crystals.

In BaTGS the growth velocity along the plane (0 1 1) was less and this was evident by the wide area of the plane. In addition the crystal has showed elongation along the b-axis as compared to the pure TGS crystal.

Incorporation of Cu$^{2+}$ as an additive in TGS has made changes in the morphology even in b and c plane. The face (0 -1 1) has wide area as compared to the faces (0 1 1), (1 1 0) and (1 0 0).

Addition of Pb$^{2+}$ has resulted a slow growth along the (0 1 1) plane. It is faster along the (1 0 1) plane. As in case of BaTGS, the elongation has occurred along the b-axis with narrowing of the faces (1 1 -1), (1 -1 -1) and (1 0 1).

The addition of trivalent impurities like Fe$^{3+}$ and Mn$^{3+}$ show a faster growth rate along the a-direction unlike the divalent impurities. The face (0 1 1) in case of FeTGS has shown a wide area while in the MnTGS the faces (1 -1 -1) and (1 1 -1) show large area. The growth along (1 0 0), (1 1 -5) and (0 1 -1) is slow in either case.
3.4(a): Pure TGS
3.4(b): BaTGS
3.4(c): CuTGS
3.4(d): PbTGS
3.4(e): FeTGS
3.4(f): MnTGS

Figure 3.4: Morphology of the pure and doped TGS crystals grown
3.4 EDAX ANALYSIS

Energy dispersive X-ray spectroscopy is an analytical technique used for the elemental analysis or chemical characterization of a sample. The EDAX instrument used in the present investigation was Philips EM 400 scanning electron microscope with an EDAX attachment.

Figure 3.5 (a) : BaTGS
Figure 3.5 (b): CuTGS

Figure 3.5 (c): PbTGS
Figure 3.5(d): FeTGS

Figure 3.5(e): MnTGS

Figure 3.5: EDAX spectrum of the crystals grown
The output of an EDX analysis is an EDX spectrum, just a plot of how frequently an X-ray is received for each energy level. The EDAX spectrum of the doped TGS crystals are shown in figures 3.5(a) – 3.5(e). The spectrum shows different peaks unique to the elements indicating the presence of different dopants in the TGS crystals grown in the present investigation.

The percentage of the dopants taken initially and the value as obtained from EDAX analysis are given in Table 3.2. The values obtained nearly agree with each other.

Table 3.2: Percentage of dopants by EDAX analysis

<table>
<thead>
<tr>
<th>Dopant</th>
<th>Ba</th>
<th>Cu</th>
<th>Pb</th>
<th>Fe</th>
<th>Mn</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial value</td>
<td>0.76</td>
<td>0.77</td>
<td>1.02</td>
<td>0.50</td>
<td>0.52</td>
</tr>
<tr>
<td>EDAX data</td>
<td>0.72</td>
<td>0.73</td>
<td>0.96</td>
<td>0.46</td>
<td>0.49</td>
</tr>
</tbody>
</table>

3.5 CONCLUSION

It is found that the optimum growth conditions of single crystals containing TGS were found to be dependent on the pH-value of the solution. For this, in the present work, the pH of the solution was maintained at 2.5. The crystal morphology of the doped TGS gets slightly modified along a- and b- axis when compared to pure TGS.

The morphology of the crystals results from the different growth of various faces, which changes gradually when the dopant is introduced in the mother solution.
characteristic form of pure TGS gets disturbed due to the influence of dopants in the solution. Increase in the concentration of the dopants reduced the size of the (0 1 0) faces and also the number of developed faces as compared to pure TGS.

The EDAX spectrum of the doped TGS crystals shows different peaks unique to the elements indicating the presence of different dopants in the TGS crystals grown. From the relative heights of the peaks in the spectrum, the concentration of the dopants have been estimated using EDAX mapping software.

REFERENCES