CHAPTER – II

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CHAPTER - II

SYNTHESIS, CRYSTAL GROWTH AND
X-RAY DIFFRACTION ANALYSIS

2.1. Introduction

Crystals have fascinated the engineers as the key materials of modern electronics, optoelectronics, quantum electronics and many solid state devices [146]. The growth of single crystals is both scientifically and technologically important and the applications of such crystals today ranges from electronics to synthetic gemstones. There is a strong connection between the optical, electrical, thermal and mechanical responses with the crystal structure is often observed and for applications, materials are used in the form of bulk crystals (three dimensional), epitaxial thin films (two dimensional) or fibre crystals (nearly one dimensional). There is great demand for single crystal in the production of solid state devices, nearly ten thousand tones of crystals are grown each year to meet the demands [147]. Though the crystal growth has been studied extensively more than ten decades, still it plays a dominant role in both theoretical and experimental research fields as well as in diversified applications [148]. Growth of a crystal is an interdisciplinary process covering Physics, Chemistry, Material Science, Chemical Engineering, Metallurgy, Crystallography, Mineralogy, etc. Growth of single crystals and their characterization towards device fabrication have assumed the great impetus due to their importance for both academic as well as applied research. Hence, in
order to achieve high performance from the device, good quality single crystals are needed.

The method of growing crystals varies widely, which is mainly dictated by the characteristics of the material and its size [149, 150]. Crystal growth is more often an art than a science and many trials are often necessary before good crystals of a given material may be produced [151]. Buckley in 1951 has elegantly stated [149], “It should be remembered that, in the preparation of large crystals, the touch of the artist is about as important as the application of established scientific principles”. The essential work of the crystal grower is to produce single crystal in large size from its poly-crystallize form by adopting appropriate technique. It remains for the crystal growers to collate the physical and chemical properties, supplement these measurements with analytical, optical and other physical instrumental measurements to deduce things relevant to the identity and position of the atoms in the crystal to characterize it [152]. This chapter explains in detail about the experimental methods adopted for the synthesis, growth and X-ray diffraction analysis of the grown crystals.

2.2. Growth from solution

Growth from solution is a popular method for growing single crystals of a number of inorganic, organic and semiorganic materials. This method is potentially very useful for growing bulk size crystals. Materials, which have high solubility and have variation in solubility with temperature, can be grown easily by solution method. Depending on the solvents and the solubility of the solute, low temperature solution growth method is adopted for the growth of crystal.
2.2.1. Low temperature solution growth

This method is widely used for the growth of single crystals, when the starting materials are unstable at high temperatures [153] and also which undergo phase transformations below melting point [154]. 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 mechanism of crystallization from solution is governed by the interaction of ions or molecules of the solute and the solvent which is based on the solubility of substance on the thermodynamical parameters of the process; temperature, pressure and solvent concentration [155]. The constant temperature bath is used to control the temperature of accuracy of ± 0.01°C. Due to this precise temperature control, supersaturation can be effectively controlled. Also efficient stirring of solutions reduces fluctuations to a minimum. Crystal growth at ambient temperature reduces the possibility of major thermal shock to the crystal both during growth and removal from the apparatus.

In the low temperature solution growth, crystals are grown from the super saturated solution. Slow evaporation method is used to produce the necessary super saturation.

2.2.2. Slow evaporation method

This method is suitable for materials which have very small temperature coefficient of stability. Also this method is very convenient, when it is possible to dissolve a large amount of material in a small volume of the solvent. Here
the solution is allowed to evaporate slowly at a fixed temperature or at ambient temperature. 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. Also during evaporation, the solution loses particles, which are weakly bound to other components, the volume of the solution decreases slowly. In almost all cases, the vapour pressure of the solvent above the solution is higher than the vapour pressure of the solute. Therefore the solvent evaporates more rapidly and the solution becomes super saturated [156]. 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 the rate of evaporation of a few mm³/ hr. The advantage of this method is that the crystals can be grown at a fixed temperature using constant temperature bath.

2.3. General scheme for growth of a crystal from solution

The following major steps are involved for crystal growth from solution:

(a) Material preparation.

(b) Solvent selection.

(c) Preparation of solution.

(d) Generation of supersaturation - The driving force.

(e) Nucleation - the birth of new crystals.

(f) Growth of crystal - incorporation of crystal forming elements.

(g) Crystal habit.

(h) Habit modifiers.
The first step in crystal growth is the purification of the material in appropriate solvents. High purity of a material is an essential prerequisite for success in crystal growth. Purification can be attained by repeated crystallization of the substance in an appropriate solvent. To obtain large quantities of purified materials, zone refining, sublimation and distillation methods are frequently used. In recrystallization process the material is dissolved in a hot solvent, and then gradually cooled down to crystallize.

Selection of a solvent is crucial for the growth of crystals from solution. Water is a popular solvent for the growth of a variety of inorganic and organic compounds. 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 or habit modifications were observed upon addition of impurities [154]. Experiments reveal that a solvent in which the compound has solubility between 10% and 60% at a given temperature is economically suitable for crystal growth. The solvent has a strong influence on the habit of crystalline materials. Therefore, the solvent must be chosen carefully for solution growth, by considering the following factors:

- Good solubility for the given solute
- A good solubility gradient
- Less viscosity
- Less volatility
- Less corrosion and non-toxicity
- Small vapour pressure

The ideal solvent yields a prismatic habit in the crystal.

A solution is a homogeneous mixture of a solute in a solvent. For the preparation of solution, it is essential to have the solubility data of the material at various temperatures. Hence, the solubility of the solute in the chosen solvent must be determined before starting the growth process [157]. Solubility of the material in a solvent decides the amount of the materials, 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.

The solubility of the material may be determined by dissolving the solute in the solvent maintained at constant temperature with continuous stirring. On reaching saturation, the equilibrium concentration of the solute may be determined gravimetrically. By repeating the above procedure for different temperature the solubility curve can then be plotted (Temperature Vs Concentration). Materials with positive temperature gradient are relatively easier to grow than the materials with negative temperature gradient.

The most important requirement for crystallization is super saturation, which is the driving force for nucleation to occur. A solution in which the concentration of the solute exceeds that of the equilibrium condition at a given temperature is known as supersaturated solution.
Nucleation is the process of generating within a metastable mother phase, the initial fragments of a new and more stable phase capable of developing spontaneously into gross fragments of the stable phase. Nucleation is initiated in a series of bimolecular collisions that forms an aggregate of a small number of molecules (‘embryos’) of the dissolved material.

Once an ordered structure is formed by nucleation, the growth units (atoms, ions or molecules) can diffuse from the surrounding super saturated solution to the surface of the nuclei and incorporate into the lattice resulting in crystal growth.

The crystal habit, or morphology, is the external shape of a crystal and is governed by the different rates of growth of the various faces that bound the crystal. The growth of certain faces may be preferred over others and the shape of the growing crystals will be determined by the presence or absence of dominant growth directions [158]. Crystals that grow nearly uniformly in all three dimensions will become cubic. If the crystals grow mainly along one plane, the habit will become tabular or plate like. Finally if the crystal grows mainly in one direction it will assume a needle-like from. In general, the slowest growing faces are those that determine the habit. The habit of a crystal can vary depending on the environment in which it is grown. A number of factors can affect the habit of a crystal. These include solvent, pH, impurities, super saturation and temperature.
Habit modifiers, either present as impurities or added deliberately, have a profound effect on growth rate of one or more faces, even at very low concentrations. These impurities can be any substance other than the material being crystallized. Therefore even the solvent from which the crystals are grown can be considered to be an impurity. If impurities are deliberately added to produce a desired morphological change, they are referred to as “additives”. By adsorbing on specific faces, impurities or additives can retard and eventually even stop growth.

2.4. Apparatus for solution growth

The basic apparatus used for solution growth technique is a constant temperature bath (CTB), which consists of a control system, thick-walled glass chamber filled with water, heating element, temperature sensor, control relay, temperature indicator, stirrer and illuminating lamp. Special care should be taken to make the control system most reliably because the process of crystal growth requires long duration and noninterruption of temperature control.

The apparatus make use of an optical heating system which is free from fluctuations in temperature generally found in ordinary water heaters. For initial heating an immersion heater of 500 W capacity is fixed at the bottom of the chamber. The system uses a contact thermometer for temperature control. The desired temperature is set in the Jumo contact thermometer. The sensor converts the variable into suitable signal that can be accepted by the controller with an on-off switch. The CTB has the provision to set and read the
temperature with an accuracy of ± 0.01°C by means of three and half segment digital display. In addition, it has the capacity of controlling the temperature with an accuracy of ± 0.01°C in the temperature range from ambient to 100°C.

2.5. Material Synthesis
2.5.1. Synthesis of L-Valine Zinc Acetate (LVZA)

The starting materials L-Valine (C₅H₁₁NO₂) and zinc acetate (Zn(CH₃COO)₂) (analytical grade reagents) were taken in the equimolar ratio. The calculated amount of L-Valine was first dissolved in double distilled water. Then zinc acetate was slowly added to the solution with continuous stirring using magnetic stirrer. The prepared homogeneous mixture of solution was let to dry at room temperature. LVZA salt was synthesized according to the reaction:

\[(CH₃-CH-CH₃-CH-NH₂-COOH) + Zn (CH₃COO)₂ → Zn [CH₃-CH-CH₃-CH-NH₃-COO].[CH₃COO]₂ \] ... (2.1)

The purity of the synthesized salt was improved by the successive recrystallization process. Care was taken during heating of the solution and a maximum temperature of 50°C was maintained in order to avoid decomposition. The melting point of LVZA salt was observed to be 216.2°C.

2.5.2. Synthesis of Glycinium Maleate (GM)

Glycinium maleate (GM) was synthesized by dissolving the analytical grade glycine and maleic acid in a stoichiometric ratio of 1:1 in an aqueous
medium. The solution was prepared with continuous stirring at a temperature slightly more than the room temperature. The prepared solution was left to dry and the GM salt was obtained. The purity of the synthesized salt was improved by successive recrystallization process and filtration. The reaction mechanism of the GM salt is as follows.

\[
C_2H_5NO_2 + C_4H_4O_4 \rightarrow C_2H_6NO_2^+.C_4H_3O_4^- ...
\]  

(2.2)

The melting point of GM salt was observed to be 143.6°C.

2.5.3. Synthesis of TriGlycine Barium Dichloride Dihydrate (TGBDD)

Trisglycine barium dichloride dihydrate (TGBDD) was synthesized by dissolving high purity analar grade glycine (NH₂CH₂COOH) and barium dichloride dihydrate (BaCl₂.2H₂O) in the ratio 3:1 in double distilled water according to the reaction,

\[
3(NH₂CH₂COOH) + BaCl₂.2H₂O \rightarrow Ba(NH₃CH₂COO)₃Cl₂.2H₂O ...
\]  

(2.3)

The calculated amount of barium dichloride dihydrate was first dissolved in double distilled water. Then the calculated amount of glycine salt was slowly dissolved in the solution with continuous stirring. The prepared solution was let to dry at room temperature. Extreme care was taken while crystallizing the salt to avoid oxidation of glycine. The solution temperature was always maintained below 50°C. Impurity content of TGBDD was minimized and the purity of the synthesized salt was improved by the successive recrystallization process. The melting point of TGBDD synthesized salt was observed to be 162.8°C.
2.5.4. Synthesis of Glycine Thiourea (GT)

Glycine thiourea (GT) was synthesized by dissolving high purity thiourea and glycine in the equimolar ratio in aqueous medium. Thiourea was first dissolved in Millipore water and then glycine was added with continuous stirring. The prepared solution was slightly heated up and the beaker containing the solution was suitably closed and the solvent was allowed to evaporate at room temperature. The product was obtained as per the following reaction.

\[
\text{CS(NH}_2\text{)}_2 + \text{NH}_2\text{CH}_2\text{COOH} \rightarrow \text{CH}_2\text{CS(NH}_2\text{)}_2\text{NH}_3^+\text{COO}^- \quad (2.4)
\]

The impurity content of GT was minimized by the process of recrystallization. The melting point of GT salt was observed to be 155.4°C.

2.5.5. Synthesis of Thiourea doped TrisGlycine Zinc Chloride (TuTGZC)

Triglycine zinc chloride (TGZC) was synthesized by dissolving high purity analar grade glycine (NH\textsubscript{2}CH\textsubscript{2}COOH) and zinc chloride (ZnCl\textsubscript{2}) in the ratio 3:1 in an aqueous medium according to the reaction

\[
3(\text{NH}_2\text{CH}_2\text{COOH}) + \text{ZnCl}_2 \rightarrow (\text{NH}_3\text{CH}_2\text{COO})_3\text{ZnCl}_2 \quad (2.5)
\]

The required volume of zinc chloride was dissolved in Millipore water. Then the calculated amount of glycine salt was slowly dissolved in the zinc chloride solution. Then 0.1 mol of the thiourea (CS(NH\textsubscript{2})\textsubscript{2}) was added. Extreme care was taken while crystallizing the salt to avoid oxidation of glycine. The solution temperature was always maintained below 50°C. Impurity content of the TuTGZC was minimized by purifying thrice by recrystallization. The melting point of TuTGZC salt was observed to be 243.8°C.
2.5.6. Synthesis of BisThiourea Sodium Nitrate (BTSN)

Bis thiourea sodium nitrate (BTSN) was synthesized from commercially available AR grade thiourea (CS(NH$_2$)$_2$) and sodium nitrate (NaNO$_3$) by mixing them in distilled water in the 2:1 ratio according to the reaction.

\[ 2[CS(NH_2)_2] + NaNO_3 \rightarrow Na[CS(NH_2)_2]_2 NO_3 \]  ... (2.6)

The calculated amount of thiourea was first dissolved in distilled water. Then sodium nitrate was added slowly to the solution with continuous stirring for six hours at temperature 40°C. The prepared solution was let to dry at the same temperature. The product was purified by repeated recrystallization process. The melting point of BTSN salt was observed to be 163.2°C.

2.5.7. Synthesis of Thiourea Potassium Magnesium Sulphate (TPMS)

TPMS salt was synthesized by dissolving thiourea (AR grade), potassium sulphate (AR grade) and magnesium sulphate hepta hydrate (AR grade) in the ratio 3:0.25:0.75 in double distilled water. The prepared solution was slightly heated up and solvent was allowed to evaporate. TPMS was synthesized as per the following reaction

\[ 3[CS(NH_2)_2] + K_2SO_4 + MgSO_4.7H_2O \rightarrow K_2Mg[CS(NH_2)_2]_3SO_4.7H_2O \]  ... (2.7)

The synthesized TPMS salt was purified by successive recrystallization processes. The melting point of TPMS salt was observed to be 216.8°C.
2.6. Solubility diagram and Growth of the crystals

The solubility test gives us idea to select the suitable solvent and temperature to grow good quality single crystals. The solubility of a material in a solvent decides the amount of the material which is available for growth and hence determines the size of the crystal that can be grown. Using the synthesized salt, a solution was prepared in double distilled water and maintained at a particular temperature with continuous stirring to ensure homogeneous temperature and concentration over the entire volume of the solution. On reaching saturation, the content of the solution was analyzed gravimetrically [159]. This procedure was repeated for every 5°C for water, ethanol and methanol in the range 30-50°C. The solubility curve was drawn between temperature and concentration. The solubility curves of LVZA, GM, TGBDD, GT, TuTGZC, BTSN and TPMS are shown in Figures 2.1 - 2.7.

It is found that all the samples exhibit a positive temperature gradient and water is found to be the best solvent to grow the single crystals by slow evaporation technique. A good solvent requires moderate solubility, positive temperature coefficient of solubility, low vapour pressure, non-flammability, low price in pure state and nontoxicity. All the crystals reported in the thesis are grown from water, as water satisfies all the requirements of a good solvent.
Fig. 2.1: Solubility curve of LVZA

Fig. 2.2: Solubility curve of GM

Fig. 2.3: Solubility curve of TGBDD
Fig. 2.4: Solubility Curve of GT

Fig. 2.5: Solubility curve of TuTGZC

Fig. 2.6: Solubility Curve of BTSN
2.6.1. Crystal growth of LVZA

Saturated solution was prepared (pH = 5.08) using recrystallized salt of LVZA with double distilled water as solvent at 35°C temperature. The prepared solution was filtered using Whatmann 41 filter paper to remove the suspended impurities. The solution was taken in beaker and covered with perforated paper. The covered beaker with saturated solution was kept in CTB at 35°C with accuracy of ± 0.01°C. LVZA single crystal of size 24 × 26 × 16 mm³ was grown by slow evaporation technique and harvested in a growth period of 25 days and is shown in Fig. 2.8.
2.6.2. Crystal growth of GM

Bulk single crystal of the GM was grown by slow evaporation technique in an aqueous solution. The calculated amount of recrystallized salt of GM was dissolved in distilled water using magnetic stirrer and the solution was saturated at 35°C. The pH value of the solution was 5.2. Then the solution was kept in a CTB controlled to an accuracy of ± 0.01°C. After that optical quality seed crystal obtained by slow evaporation method was suspended in the growth solution. The bath temperature was maintained at 35°C. Optically good single crystal of dimension 14 × 7 × 8 mm³ was obtained within a period of 20 days as shown in Fig. 2.9.

Fig. 2.9: Photograph of as - grown crystal of GM

2.6.3. Crystal growth of TGBDD

Saturated solution (pH = 4.9) was prepared using recrystallized salt of TGBDD with double distilled water as solvent at temperature 35°C. The prepared solution was filtered using 0.2 μm porosity filter papers to remove the suspended impurities after suitable preheating. The solution was taken in beaker and covered with perforated paper. The covered beaker with saturated
solution was kept in CTB at 35°C with accuracy of ± 0.01°C. TGBDD single crystals were grown by slow evaporation technique. Transparent and good optical quality single crystals (13 × 12 × 9 mm³) were harvested after 30 days and the photograph of the grown crystals is shown in Fig. 2.10.

Fig. 2.10: Photograph of as - grown crystals of TGBDD

2.6.4. Crystal growth of GT

Bulk single crystals of GT were grown by slow evaporation technique from aqueous solution. The saturated solution (pH = 4.8) prepared at 30°C was filtered and taken in a beaker and closed with a parafilm and was kept in a CTB maintained at 30°C. The solvent was allowed to evaporate slowly. Single crystals of GT (8 × 7 × 7 mm³) obtained in a growth period of 20 days are shown in Fig. 2.11.

Fig. 2.11: Photograph of as - grown crystals of GT
2.6.5. Crystal growth of TuTGZC

Saturated solution of TuTGZC (pH = 5.1) was prepared using synthesized salt in double distilled water. The final saturated solution was filtered using 0.2 µm porosity filter papers after suitable preheating. The solution was kept in beaker covered with perforated sheet and loaded in the CTB set at 35°C. Slow evaporation solution growth method was employed for the growth. Transparent and good quality grown crystal was harvested after 25 days with size 25 × 10 × 10 mm³ and is shown in Fig. 2.12.

Fig. 2.12: Photograph of as - grown crystal of TuTGZC

2.6.6. Growth of BTSN crystal

The synthesized salt of BTSN was dissolved in distilled water and thoroughly mixed using a magnetic stirrer to ensure homogeneous concentration throughout the volume of the solution. The pH value of the solution was 4.9 at 30°C temperature. The saturated solution prepared at 30°C was taken in a beaker, covered with perforated paper and placed in the CTB at 30°C and left undisturbed for slow evaporation. Good quality single crystal of BTSN of size 14 × 8 × 7 mm³ were grown in 30 days and is shown in Fig. 2.13.
2.6.7. Crystal growth of TPMS

The saturated solution of TPMS (pH = 4.8) prepared at 35°C was filtered using Whatman filter paper. The filtered solution was taken in the beaker and closed with perforated cover and was kept in a CTB maintained at 35°C. The solvent was allowed to evaporate slowly. TPMS crystal of size $20 \times 25 \times 10 \text{ mm}^3$ was harvested from the mother solution with a time span of 30 days. The grown TPMS crystal is shown in Fig. 2.14.
2.7. X-Ray diffraction (XRD) analysis

In crystalline substance, the smallest volume element is called a unit cell. The unit cell can contain a single atom or atoms in a fixed arrangement. The dimensions of the unit cell is described by three axes: a, b, c (lengths) and angles between a, b, c are alpha (α), beta (β) and gamma (γ). The unit cell dimensions are called lattice constants or parameters which can be determined by XRD. Diffraction in crystal occurs only when Bragg’s law is satisfied. Condition for constructive interference from planes with spacing ‘d’ is,

\[ 2dsin\theta = n\lambda \]

where \( \theta \) is the glancing angle, \( \lambda \) is the wavelength of X-rays used and \( n \) is the order of diffraction. Using X-ray diffraction principle, two techniques are generally used to get information of size and shape of the unit cell of a crystal. They are:

1. Single crystal XRD

Single crystal X-ray diffraction method is a non-destructive analytical technique which provides a convenient and practical means for the qualitative indentification of the crystalline compounds, especially the precise determination of unit cell parameters. The grown crystals were subjected to single crystal XRD using an ENRAF NONIUS CAD-4 diffractometer with Mo K\(_\alpha\) (\( \lambda = 0.71073\AA \)) radiation to estimate the lattice parameter. A single crystal was mounted on a thin glass fibre on a goniometer head. The unit cell dimensions and the orientation matrix were determined using 25 reflections and then the intensity data of a given set of reflections were collected.
2. Powder crystal XRD

Powder XRD method is one of the powerful tool to identify and characterize a new material. It is a unique analytical method capable of providing qualitative and quantitative information about the crystal in powder form. PXRD tests are performed mainly to verify the crystalline nature of the grown crystals. Powder XRD analysis was carried out for the powder samples of the grown crystals using a Rich Seifert diffractometer with Cu $K_{\alpha}$ ($\lambda = 1.54059\text{Å}$) radiation.

2.7.1. Single crystal XRD analysis of LVZA

Lattice parameters of LVZA crystal were obtained by single crystal XRD analysis. These lattice parameters are compared with L-Valine [160] and shown in Table 2.1. From this study it was found that the LVZA crystallizes in monoclinic system ($\beta = 112.73^\circ$). The volume of the cell is $792\text{Å}^3$.

<table>
<thead>
<tr>
<th>Samples</th>
<th>a (Å)</th>
<th>b (Å)</th>
<th>c (Å)</th>
<th>$\beta$ (°)</th>
<th>Unit Cell Volume (Å$^3$)</th>
<th>Crystal System</th>
</tr>
</thead>
<tbody>
<tr>
<td>L-Valine [160]</td>
<td>9.701</td>
<td>5.261</td>
<td>11.953</td>
<td>90.66</td>
<td>610</td>
<td>Monoclinic</td>
</tr>
<tr>
<td>LVZA Present work</td>
<td>10.02</td>
<td>6.43</td>
<td>13.33</td>
<td>112.73</td>
<td>792</td>
<td>Monoclinic</td>
</tr>
</tbody>
</table>
2.7.2. Single crystal XRD analysis of GM

The unit cell parameters are obtained by single crystal X-ray diffraction analysis and compared with the reported values in Table 2.2. In glycinnium maleate, the glycine molecule exists in the cationic form with a positively charged amino group and an uncharged carboxylic acid group. The maleic acid molecule exists in a mono-ionized state. In the semi maleate ion, an intramolecular OH…O hydrogen bond is found to be asymmetric [114]. A C-H…O hydrogen bond is also observed. The glycinnium and semi maleate ions aggregate into alternate columns extending along the c-axis.

<table>
<thead>
<tr>
<th>Samples</th>
<th>a (Å)</th>
<th>b (Å)</th>
<th>c (Å)</th>
<th>β (°)</th>
<th>Unit Cell Volume (Å³)</th>
<th>Crystal System</th>
</tr>
</thead>
<tbody>
<tr>
<td>GM Rajagopal et al. [114]</td>
<td>17.689</td>
<td>5.610</td>
<td>17.328</td>
<td>112.30</td>
<td>1605.4</td>
<td>Monoclinic</td>
</tr>
<tr>
<td>GM Present work</td>
<td>17.77</td>
<td>5.62</td>
<td>17.24</td>
<td>112.70</td>
<td>1588</td>
<td>Monoclinic</td>
</tr>
</tbody>
</table>

2.7.3. Single crystal XRD analysis of TGBDD

Single crystal X-ray diffraction analysis shows that TGBDD crystallizes in orthorhombic system. The obtained cell parameters of TGBDD crystal are \( a = 8.26\,\text{Å}, b = 9.29\,\text{Å}, c = 14.82\,\text{Å}, \alpha = \beta = \gamma = 90° \) and volume = 1137 Å³.

2.7.4. Single crystal XRD analysis of GT

Single crystal XRD study reveals that GT belongs to monoclinic crystal system. The observed lattice parameters of GT are compared with that of glycine (\( \alpha,\gamma \)) and thiourea (TU) [161] in Table 2.3.
Table 2.3: Comparison of lattice parameters of Glycine, TU and GT

<table>
<thead>
<tr>
<th>Samples</th>
<th>a (Å)</th>
<th>b (Å)</th>
<th>c (Å)</th>
<th>Angle</th>
<th>Crystal system</th>
<th>Melting Point (°C)</th>
<th>Unit cell Volume (Å³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>α-glycine</td>
<td>5.197</td>
<td>12.071</td>
<td>5.474</td>
<td>β=112.91°</td>
<td>Monoclinic</td>
<td>226.8</td>
<td>315.01</td>
</tr>
<tr>
<td>[162]</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>γ-glycine</td>
<td>7.004</td>
<td>7.004</td>
<td>5.447</td>
<td>α=β=γ=90°</td>
<td>Hexagonal</td>
<td>178.9</td>
<td>231.46</td>
</tr>
<tr>
<td>[162]</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>TU</td>
<td>7.66</td>
<td>8.54</td>
<td>5.52</td>
<td>α=β=γ=90°</td>
<td>Orthorhombic</td>
<td>176.0</td>
<td>360.73</td>
</tr>
<tr>
<td>[161]</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>GT Present work</td>
<td>5.32</td>
<td>11.90</td>
<td>5.85</td>
<td>β =95.78°</td>
<td>Monoclinic</td>
<td>156.3</td>
<td>370</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

2.7.5. Single crystal XRD analysis of TuTGZC

Single crystal X-ray diffraction study was performed for the grown TGZC and TuTGZC crystals. Both TGZC and TuTGZC crystal belong to orthorhombic system (α = β = γ = 90°). Lattice parameter values of TGZC and TuTGZC are compared in Table 2.4. This analysis revealed that the induction of thiourea ligand in the TGZC crystal does not change the crystal system though there is a small change in the lattice parameters.

Table 2.4: Lattice parameters of TGZC and TuTGZC crystals

<table>
<thead>
<tr>
<th>Samples</th>
<th>a (Å)</th>
<th>b (Å)</th>
<th>c (Å)</th>
<th>Unit Cell Volume (Å³)</th>
<th>Crystal System</th>
</tr>
</thead>
<tbody>
<tr>
<td>TGZC [105]</td>
<td>11.230</td>
<td>15.251</td>
<td>15.564</td>
<td>2666</td>
<td>Orthorhombic</td>
</tr>
<tr>
<td>TGZC Present work</td>
<td>11.14</td>
<td>15.16</td>
<td>15.48</td>
<td>2614</td>
<td>Orthorhombic</td>
</tr>
<tr>
<td>TuTGZC Present work</td>
<td>11.10</td>
<td>15.15</td>
<td>15.38</td>
<td>2586</td>
<td>Orthorhombic</td>
</tr>
</tbody>
</table>
2.7.6. Single crystal XRD analysis of BTSN

Single crystal XRD study reveals that BTSN belongs to monoclinic crystal system ($\beta = 90.13^\circ$). In order to reveal the role of metal ions with thiourea complexes, a comparison is made between the cell parameters of thiourea (TU), bisthiourea cadmium chloride (BTCC), bisthiourea zinc chloride (BTZC), zinc thiourea sulphate (ZTS), bisthiourea sodium fluoride (BTSF) with bisthiourea sodium nitrate in Table 2.5.

**Table 2.5: Comparison of lattice parameters of TU, BTCC, BTZC, ZTS, BTSF and BTSN**

<table>
<thead>
<tr>
<th>Samples</th>
<th>a (Å)</th>
<th>b (Å)</th>
<th>c (Å)</th>
<th>Unit Cell Volume ($\text{Å}^3$)</th>
<th>Crystal System</th>
</tr>
</thead>
<tbody>
<tr>
<td>TU [161]</td>
<td>7.66</td>
<td>8.54</td>
<td>5.52</td>
<td>360.7</td>
<td>Orthorhombic</td>
</tr>
<tr>
<td>BTZC [133]</td>
<td>5.901</td>
<td>12.751</td>
<td>12.977</td>
<td>976.5</td>
<td>Orthorhombic</td>
</tr>
<tr>
<td>ZTS [137]</td>
<td>11.111</td>
<td>7.792</td>
<td>15.478</td>
<td>1340.1</td>
<td>Orthorhombic</td>
</tr>
<tr>
<td>BTSN Present work</td>
<td>7.64</td>
<td>5.47</td>
<td>8.54</td>
<td>357</td>
<td>Monoclinic</td>
</tr>
</tbody>
</table>

2.7.7. Single crystal XRD analysis of TPMS

Single crystal X-ray diffraction shows that the crystal TPMS belongs to orthorhombic system. The observed unit cell parameters are given in Table 2.6 and compared with tristhiourea magnesium sulphate [139].
Table 2.6: Comparison of lattice parameters of TPMS with MTS

<table>
<thead>
<tr>
<th>Samples</th>
<th>a (Å)</th>
<th>b (Å)</th>
<th>c (Å)</th>
<th>Unit Cell Volume (Å³)</th>
<th>Crystal System</th>
</tr>
</thead>
<tbody>
<tr>
<td>MTS [139]</td>
<td>5.482</td>
<td>7.672</td>
<td>8.562</td>
<td>360</td>
<td>Orthorhombic</td>
</tr>
<tr>
<td>TPMS Present work</td>
<td>7.79</td>
<td>11.17</td>
<td>15.50</td>
<td>1349</td>
<td>Orthorhombic</td>
</tr>
</tbody>
</table>

2.7.8. Powder XRD analysis of the grown crystals

X-ray diffraction pattern was recorded by crushing the grown crystal into fine powder and the powder sample was scanned over the 2θ range 10-80° at a rate of 1° per minute. All the reflection planes are identified and the obtained 2θ values are used for indexing using Check cell software package. The indexed powder X-ray diffraction pattern of the LVZA, GM, TGBDD, GT, TuTGZC, BTSN and TPMS crystals are shown in Figs. 2.15 - 2.21. The well defined and sharp peaks imply the good crystalline nature of the compounds.

Fig. 2.15: Powder XRD spectrum of LVZA
Fig. 2.16: Powder XRD spectrum of GM

Fig. 2.17: Powder XRD spectrum of TGBDD

Fig. 2.18: Powder XRD spectrum of GT
Fig. 2.19: Powder XRD spectrum of TuTGZC

Fig. 2.20: Powder x-ray diffraction spectrum of BTSN

Fig. 2.21: Powder XRD pattern of TPMS
2.8. Conclusion

Thus, L-Valine, glycine and thiourea based NLO materials LVZA, GM, TGBDD, GT, TuTGZC, BTSN and TPMS were synthesized. It was found that all the synthesized salts exhibit a positive temperature gradient and water was found to be more suitable solvent. Bulk single crystals were grown from aqueous solution by slow evaporation method. Single crystal X-ray diffraction analysis conveyed that the LVZA, GM, GT, BTSN were crystallized in monoclinic system and TGBDD, TuTGZC, TPMS crystallized in orthorhombic system. Lattice parameters of all the grown crystals were found and compared with the relevant literature. All the reflection planes were identified from PXRD spectrum. The indexed powder XRD pattern of all the grown crystals showed the well defined sharp peaks which conveyed the good crystalline nature.