Chapter - VI

Growth and Characterization of Urea L-Malic Acid and Tris(thiourea) Zinc Sulphate Crystals
6.1 Introduction

The development of highly efficient nonlinear optical materials for opto-electronic applications such as high speed information processing, optical modulators and frequency doubling devices have been the subject of intense research activity over the past two decades [1,2]. Organic NLO materials are generally more versatile than their inorganic counterparts due to their more favourable nonlinear response since these are often formed by weak Van der Waals and hydrogen bonds and hence possess a high degree of delocalization [3]. It is necessary to use the molecules with high molecular hyperpolarizability (β) and to form an acentric crystal structure to obtain crystals with high second order nonlinear susceptibility (χ²). Molecular salts composed of a cation with high β and a counter–anion to improve the alignment of the molecules have been reported [4]. Such molecular salts are the promising SHG crystals for three reasons. Firstly, enhancement of β is expected by a change in the electronic state due to the introduction of a
positive charge. Secondly, the crystal might exhibit an acentric structure and thirdly, the physical properties necessary for device developments such as high crystallinity and high melting point can be attained. Although such approaches are promising, not all combinations of cation and anion always give high $\chi^2$, because the molecules are apt to align symmetrically. There are many methods for the alignment of the molecules into an acentric structure, for example, the introduction of the chiral centres or intermolecular hydrogen bonds [4]. Watanabe et al. have reported the 2-amino-5-nitropyridine L- (+)-tartrate with SHG efficiency 9 times of urea. Wento et al. [5] have reported the crystal structure of urea -(+) tartaric acid. The asymmetric unit in the structure contains an urea and a (+) tartaric acid molecule, which are connected by strong O-H—O hydrogen bond. The packing of the molecule in the crystal is stabilized by a three dimensional network of hydrogen bonds. L-malic acid is used to create a two dimensional anionic network held together by O-H—O hydrogen bonds. It has SHG efficiency three times greater than that of KDP [5,6]. However, in general, the organic NLO materials have low thermal and mechanical stability thereby discounting many possible applications.

Presently, extensive research in the field of nonlinear optics has revealed that the metal complexes of highly polarizable organic molecules, known as metal-organics, possess favourable physical
properties such as high laser damage threshold, improved mechanical hardness and thermal stability due to the combination of both organic and inorganic constituents. The metal coordination compounds formed by the organic ligands like thiourea [7], allyl thiourea [8] and thiosemicarbazide [9] with metal ions (Zn, Cd and Hg) have been identified as type II semiorganic compounds and they are based on the idea of introducing an asymmetric conjugated organic molecule into an inorganic distorted polyhedra. In these complexes, the central metal atom acts as a bridge for charge transfer, increasing the susceptibility of the individual units because of the strong coordination in the vertical conjugation planes. Among the organic ligands, thiourea with its resonance structure (Fig. 6.1) possesses a large dipole moment and it forms a number of coordination compounds such as bis(thiourea)zinc chloride (BTZC) [10], bis(thiourea)cadmium chloride (BTCC) [11], tris(thiourea) zinc sulphate (ZTS) etc. [12]. They are the potential materials for frequency doubling of the near IR laser radiation. Thiourea itself crystallizes in a centrosymmetric space group Pbnm and the architecture of introducing an inorganic component into the organic crystal to break the centrosymmetry was a novel idea and with zinc sulphate, the resulting complex ZTS crystallizes in the noncentrosymmetric space group Pca2₁. Semiorganic NLO materials
have high thermal, mechanical and optical properties compared with organic materials.

\[
\text{Fig. 6.1 Resonance structure of thiourea molecule.}
\]

6.2 Review of Earlier Work

Dixit et al. [13] have reported the crystal growth, mechanical and dielectric studies of urea L-malic acid (ULMA). It crystallizes in the monoclinic space group P2₁ with unit cell parameters \( a = 9.0335\ (8) \) Å, \( b = 6.9356\ (5) \) Å, \( c = 6.8008\ (6) \) Å, \( \beta = 94.67(0) \) and \( Z = 2 \). Gomes et al. [6] have reported the crystal growth and nonlinear optical studies of ULMA.

Marcy et al. [14] have shown that the second harmonic conversion efficiency of ZTS is comparable to that of potassium dihydrogen phosphate (KDP). Venkataraman et al. [15] have reported the crystal growth and vibrational spectral analysis of ZTS. Ushashree et al. [16,17] have investigated the different aspects of crystal growth of ZTS. Recently, many more investigations have thrown light on the
electro-optic effect, phase transition and surface anisotropy of this interesting material. Vasantha et al. [18] have reported the EPR and optical absorption studies of VO$^{2+}$ doped ZTS.

6.3 Present Investigations

In the present investigation, attempts have been made to synthesize and grow single crystals of ULMA and ZTS with considerable size suitable for NLO applications. The grown crystals have been characterized by structural, thermal, mechanical and optical (linear and nonlinear) studies. The results of these investigations of ZTS have already been published by the author [19].

6.4 Synthesis and Solubility

ULMA (CO(NH$_2$)$_2$C$_4$H$_6$O$_5$) was synthesized from urea and L-malic acid taken in the equimolar ratio. The reaction is as follows:

$$\text{CO(NH}_2\text{)}_2 + \text{C}_4\text{H}_6\text{O}_5 \rightarrow \text{CO(NH}_2\text{)}_2\text{C}_4\text{H}_6\text{O}_5$$  \hspace{1cm} (6.1)

The calculated amount of the reactants was thoroughly dissolved in double distilled water and stirred well using a magnetic stirrer. The resulting solution was evaporated to dryness at 55°C in a temperature controlled water bath to avoid any possible decomposition. The synthesized colourless crystalline salt of ULMA was obtained with the yield of 95% with the melting point 118°C.
ZTS was synthesized from thiourea and zinc sulphate following the reaction

$$\text{ZnSO}_4 + 3\text{CS(NH}_2)_2 \rightarrow \text{Zn[CS(NH}_2)_2]_3\text{SO}_4$$  \hspace{1cm} (6.2)

Thiourea and zinc sulphate (3:1 ratio) were dissolved in double distilled water and the solution was thoroughly stirred using a magnetic stirrer. A white crystalline salt of ZTS was formed immediately (with the yield of 90%) and purified by the repeated recrystallization process in double distilled water. The melting point of the synthesized material is 233°C.

ULMA was dissolved in double distilled water and maintained at 30°C with continuous stirring using a magnetic stirrer to ensure the homogeneity of temperature and concentration over the entire volume of the solution. On reaching saturation, the content of the solution was analyzed gravimetrically and this process was repeated for every 5°C in ethanol in the temperature range 30°C-50°C [Fig.6.2]. By adopting the foregoing procedure the solubility of ZTS was also determined in water, water mixed ethanol (1:1) and ethanol [Fig. 6.3]. The solubility of both compounds was found to be very high in water than ethanol.
Fig. 6.2 Solubility curves of ULMA.

Fig. 6.3 Solubility curves of ZTS.
ULMA was dissolved thoroughly in double distilled water using a magnetic stirrer. A saturated solution was prepared at 30°C with pH 4.2 and kept for slow evaporation to grow good quality single crystals. After 30 days, single crystals of size $10 \times 8 \times 3 \text{ mm}^3$ have been harvested from the mother solution (Fig. 6.4).

A saturated aqueous solution of ZTS was prepared at 30°C with pH 4.17 and 3.80, and the solution was kept for slow evaporation. Good quality single crystals with regular shape and size $10 \times 6 \times 5 \text{ mm}^3$ and $14 \times 10 \times 4 \text{ mm}^3$ were grown within three weeks with an approximate growth rate of 0.5 mm/day with respective pH values (Figs. 6.5a & 6.6a). The growth rate in (100) and (010) planes is larger than in the other planes.

Fig. 6.4 As grown single crystals of ULMA.
Fig. 6.5(a) As grown crystal of ZTS (b) Morphology of ZTS (pH=4.17).

Fig. 6.6(a) As grown crystal of ZTS (b) Morphology of ZTS (pH=3.8).
6.5 Characterization
6.5.1 X-ray Single Crystal Diffraction

Single crystals of ULMA and ZTS were subjected to X-ray diffraction using an Enraf Nonious CAD4 X-ray diffractometer with MoKα radiation (λ = 0.7107 Å) to determine the unit cell dimensions and morphology. A single crystal of size 0.2 x 0.2 x 0.2 mm³ was mounted on a four-circle goniometer and 25 reflections were collected. ULMA and ZTS crystals belong to monoclinic and orthorhombic systems respectively. The unit cell dimensions are presented in the table 6.1. The observed values are in good agreement with the reported values [13,18]. Reflections from a few planes were collected and indexed for the grown ZTS crystals (pH = 4.17 and 3.8, Figs. 6.5b and 6.6b).

Table 6.1 Unit cell dimensions.

<table>
<thead>
<tr>
<th>Cell dimensions</th>
<th>ULMA</th>
<th>ZTS</th>
</tr>
</thead>
<tbody>
<tr>
<td>a (Å)</td>
<td>9.0317 (8)</td>
<td>7.9780 (4)</td>
</tr>
<tr>
<td>b (Å)</td>
<td>9.9421 (5)</td>
<td>11.4345 (5)</td>
</tr>
<tr>
<td>c (Å)</td>
<td>6.8147 (6)</td>
<td>15.8757 (5)</td>
</tr>
<tr>
<td>α (°)</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>β (°)</td>
<td>94</td>
<td>90</td>
</tr>
<tr>
<td>γ (°)</td>
<td>90</td>
<td>90</td>
</tr>
<tr>
<td>V (Å³)</td>
<td>754.07</td>
<td>1410.05</td>
</tr>
</tbody>
</table>
6.5.2 FT-IR Spectral Analysis

Infrared spectroscopy is effectively used to confirm the molecular structure of the synthesized compounds. The FT-IR spectrum was recorded for ULMA and ZTS using a JASCO 460 Plus FT-IR spectrometer by KBr pellet technique in the range 400–4000 cm\(^{-1}\) (Figs. 6.7 & 6.8).

In the FT-IR spectrum of ULMA (Fig. 6.7), the intense broad band at 3396 cm\(^{-1}\) is indicative of the presence of amino groups and an equally intense band at 1721 cm\(^{-1}\) is assigned to the carbonyl stretching vibrations of the compound [20,21]. In Fig. 6.8, the symmetric and asymmetric C=S stretching vibrations at 740 cm\(^{-1}\) and 1417 cm\(^{-1}\) of thiourea are shifted to lower frequencies 717 cm\(^{-1}\) and 1404 cm\(^{-1}\) respectively in ZTS [22]. The N-H absorption bands in the high frequency region 3000–3400 cm\(^{-1}\) in thiourea [23] were not shifted to lower frequencies on the formation of metal-thiourea complex. It indicates that the nitrogen to zinc bond is not present and that the bonding must be between sulfur and zinc atoms [24]. The band at 1515 cm\(^{-1}\) is assigned to N-C-N stretching vibrations and the other characteristic vibrational frequencies are assigned in Table 6.2.

The vibrational band at 2200 cm\(^{-1}\) in ULMA was assigned to C-H stretching.
Fig. 6.7 FT-IR spectrum of ULMA.

Fig. 6.8 FT-IR spectrum of ZTS.
Table 6.2 FT-IR spectral assignments of ULMA and ZTS.

<table>
<thead>
<tr>
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<tr>
<td>......</td>
<td>......</td>
<td>411</td>
<td>424</td>
<td>N-C-N bending</td>
</tr>
<tr>
<td>......</td>
<td>......</td>
<td>469</td>
<td>474</td>
<td>C-S-N bending</td>
</tr>
<tr>
<td>596</td>
<td>546</td>
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<td>......</td>
<td>C-N bending</td>
</tr>
<tr>
<td>......</td>
<td>648</td>
<td>......</td>
<td>......</td>
<td>C-H out of plane bending</td>
</tr>
<tr>
<td>......</td>
<td>......</td>
<td>740</td>
<td>717</td>
<td>C-S sym. stretching</td>
</tr>
<tr>
<td>......</td>
<td>792</td>
<td>......</td>
<td>......</td>
<td>C-H bending</td>
</tr>
<tr>
<td>1154</td>
<td>1196</td>
<td>1089</td>
<td>1126</td>
<td>C-N stretching</td>
</tr>
<tr>
<td>......</td>
<td>......</td>
<td>1417</td>
<td>1404</td>
<td>C=S stretching</td>
</tr>
<tr>
<td>1620</td>
<td>1626</td>
<td>1627</td>
<td>1633</td>
<td>C=O stretching</td>
</tr>
<tr>
<td>3021</td>
<td>3126</td>
<td>3167</td>
<td>3206</td>
<td>C-H stretching</td>
</tr>
<tr>
<td>3413</td>
<td>3396</td>
<td>3376</td>
<td>3378</td>
<td>N-H stretching</td>
</tr>
</tbody>
</table>

6.5.3 Thermal Analyses

6.5.3.1 Thermogravimetric (TG) and Differential Thermal (DT) Analyses

The TG and DT analyses were carried out for ULMA and ZTS using a Seiko thermal analyzer. A ceramic crucible was used for heating the sample and the analyses were carried out in nitrogen atmosphere at a heating rate of 20°C/min in the temperature range 30°-800°C (Fig.6.9). The endothermic peak in the DTA curve at 118°C represents the melting point of ULMA with no phase transition. The absence of water of crystallization is indicated by the absence of a weight loss around 100°C. After 118°C, there is decomposition, illustrated by the loss of mass in the temperature range 150°-240°C where gaseous
fragments like carbon dioxide and ammonia might have been liberated. The thermal stability beyond this range is reduced due to the step-by-step decomposition of the compound and the residue (10%) was obtained at 700°C.

![Fig.6.9 TGA and DTA curves of ULMA.](image)

The DTA curve (Fig.6.10) shows that ZTS melts at 233°C and it undergoes an endothermic transition around 248°C due to the decomposition of the compound. The TGA curve indicates that there is a weight loss of about 41.82% in the temperature range 236°C-268°C due to the liberation of volatile substances probably sulphur oxide. There is no endothermic or exothermic transition beyond 400°C in the DTA curve whereas TGA shows almost a complete weight loss and the residual weight 25% was obtained at 800°C.
6.5.3.2 Differential Scanning Calorimetry Analyses

The DSC and specific heat analyses were performed for ULMA single crystal in the temperature range 25°C-100°C at a heating rate of 2°C/min in nitrogen atmosphere using a TA instruments (2920 Modulated DSC). A small piece (4 x 3 x 1 mm³) of the grown crystal was encased in the aluminum pan with a special care. In order to maintain the accuracy of the measurement, the temperature and heat flux scale of the calorimeter were calibrated. The specific heat of the ULMA is 0.8973 J/g°C at 50°C. The DSC curve shows that there is no phase transition upto 100°C. The DSC and the specific heat curves are shown in Fig.6.11. The above procedure was followed to determine the
specific heat of ZTS which is 1.232 J/g°C at 40°C (Fig.6.12). It shows that the specific heat increases with temperature and there is no phase transition upto 180°C.

Fig. 6.11 DSC and specific heat curves of ULMA.

Fig. 6.12 DSC and specific heat curves of ZTS.
Table 6.3 Comparison of melting point and specific heat.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Melting point (°C)</th>
<th>Specific heat (J/g/°C)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Urea L-malic acid</td>
<td>118</td>
<td>0.8973</td>
<td>*</td>
</tr>
<tr>
<td>Tris(thiourea) zinc sulphate</td>
<td>233</td>
<td>1.237</td>
<td>*</td>
</tr>
<tr>
<td>L-histidine diphosphate</td>
<td>185</td>
<td>1.417</td>
<td>#</td>
</tr>
<tr>
<td>L-histidine bromide</td>
<td>162</td>
<td>1.340</td>
<td>#</td>
</tr>
</tbody>
</table>

* Present work; # Chapter - IV.

6.5.4 Determination of Microhardness

Physically hardness is the resistance offered by a material to the localized deformations caused by scratching or by indentations [25,26]. The indentation hardness is measured as the ratio of applied load to the surface area of the indentation. The grown crystal of ZTS (10×8×6 mm³) with the smooth and dominant (100) plane was selected. Indentations were carried out using Vickers indentor for varying loads (P = 5-50 g). For each load, the average diagonal length (d) for different indentations was used to calculate the microhardness. Vicker’s microhardness number was determined using the relation

\[ H_v = \frac{1.8544P}{d^2} \]  

(6.3)

The hardness number was found to increase with the load. A plot between the hardness value and their corresponding loads is shown in Fig. 6.13.
Fig. 6.13 Variation of hardness with load.

The work hardening coefficient \( (n) \) of the material is related to the load \( (P) \) by the relation

\[
P = a d^n
\]  

(6.4)

where 'a' is an arbitrary constant. The plot \( \log P \) vs \( \log d \) is a straight line (Fig.6.14). The work hardening coefficient 'n' is found to be 5.3 and ZTS has a higher mechanical strength than LAP (2.0) [27].

Fig. 6.14 Plot of \( \log P \) vs \( \log d \).
6.5.5 UV-Vis Transmittance Spectral Study

The UV – Vis spectral studies were carried out for ULMA and ZTS using a Varian Cary 5E UV – Vis spectrometer in the range 200–800 nm (Figs. 6.15 & 6.16). ULMA and ZTS have a good optical transmittance in the entire visible region with the lower cutoff wavelength at 220 nm and 250 nm respectively. The large transmission in the entire visible region enables them to be the good candidates for optoelectronic applications.

Fig.6.15 UV-Vis transmittance spectrum of ULMA.
Fig. 6.16 UV-Vis transmittance spectrum of ZTS.

6.5.6 Measurement of Refractive Index

Refractive index of the crystal bears a definite relation to the crystallographic symmetry of biaxial crystals and magnitudes of the index of refraction intimately related to its structure. The refractive index of the grown crystals was determined by Brewster angle technique (Chapter-II) using a He-Ne laser (\( \lambda = 632.8 \) nm). The refractive index of ULMA and ZTS is 1.48 and 1.53 respectively.

6.5.7 Determination of Birefringence—Interference Technique

Birefringence is defined as the double refraction of light in a transparent molecularly ordered material, which is manifested by the
existence of orientation dependent differences in the refractive index. The birefringence of ZTS was measured by interference method [28] using a halogen lamp (500 W) as a source. The polarizer and the analyzer were placed in crossed positions and the crystal (thickness–mm) was placed with its optical axis perpendicular to the incident ray. When the crystal was introduced between the polarizer and the analyzer, the transmitted light from the analyzer undergoes interference and the pattern was observed through a spectrometer. To measure the birefringence as a function of temperature an electric furnace (400°C) with accuracy ±1°C (Chapter-II) was used. The birefringence was determined in the temperature range 30°C-150°C for every 40°C. The birefringence $\Delta n$ is calculated from these interference fringes using the relation

$$\Delta n = \frac{\lambda_2 - \lambda_1}{(\lambda_2 - \lambda_1)t}$$

(6.5)

where $\lambda_1$ and $\lambda_2$ are the successive wavelengths of the fringes and $t$ is the thickness of the crystal. Data analyses were performed using Microcal origin 6.0. The birefringence of ZTS as a function of temperature is shown in Fig.6.17.
Fig. 6.17 Birefringence of ZTS in the temperature range 30°-150°C.

Table 6.4 Comparison of birefringence with other NLO materials.

<table>
<thead>
<tr>
<th>Sl. No.</th>
<th>Samples</th>
<th>Birefringence</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Tris(thiourea) zinc sulphate</td>
<td>0.16</td>
<td>*</td>
</tr>
<tr>
<td>2</td>
<td>L-histidine tetrafluoroborate</td>
<td>0.15</td>
<td>#</td>
</tr>
<tr>
<td>3</td>
<td>L-histidine diphosphate</td>
<td>0.11</td>
<td>#</td>
</tr>
<tr>
<td>4</td>
<td>Potassium dihydrogen phosphate</td>
<td>0.10</td>
<td>[2]</td>
</tr>
<tr>
<td>5</td>
<td>Lithium niobate</td>
<td>0.16</td>
<td>[2]</td>
</tr>
</tbody>
</table>

* Present work, # Chapter - IV.
6.5.8 Second Harmonic Generation (SHG) Efficiency

The SHG conversion efficiency of ULMA was determined following the Kurtz and Perry technique [29] using an Nd:YAG (1064 nm, 8 ns, 10 Hz). The sample was ground and sieved into different particle sizes (<106, 106-125, 125-150, >150 μm). The powdered samples were packed tightly into the separate microcapillary tubes of uniform bore of about 1.5 mm diameter. The laser power incident on the capillary tube is 6 mJ. The SHG at 532 nm (green light) was collected by the photomultiplier tube (PMT). The optical signal incident on the PMT was converted into voltage output in the CRO. The powder SHG efficiency of ULMA is 0.45 times that of a well-known organic NLO material urea. The measurement for various particle sizes shows that SHG intensity increases with particle size (Fig. 6.18) thus giving a proof for the phase matching property of ULMA. The powder SHG efficiency of ZTS was also determined by adopting the foregoing procedure. It reveals that it has a powder SHG efficiency of 0.20 times that of urea and it is phase matchable (Fig.6.19).

Ungraded urea sample was used as reference in the powder SHG efficiency measurement for all the materials. The reference sample urea was hold in a same sample holder and was not changed physically for every experiments.
Fig. 6.18 Phase matching curve of ULMA.

Fig. 6.19 Phase matching curve of ZTS.
6.5.9 Measurement of Laser Damage Threshold

The measurement of laser damage threshold was carried out using a Quanta Ray Q-Switched Nd:YAG laser (1064 nm, 10 Hz, 10ns). The laser beam was focused by a lens on the surface of the grown ULMA crystal (size 12 x 6 x 3 mm$^3$). The damage was observed and the energy of the laser beam was measured by Scientech power meter (Model No.ACX5004). The laser damage threshold value was calculated from this laser energy divided by the focused beam area. The above procedure was followed to find out the laser damage threshold of ZTS. The laser damage threshold values are compared with other NLO materials (Table 6.5).

Table 6.5 Comparison of laser damage threshold with similar materials.

<table>
<thead>
<tr>
<th>Sl. No.</th>
<th>Samples</th>
<th>Laser damage threshold (MW/cm$^2$)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Urea L-malic acid</td>
<td>86.71</td>
<td>*</td>
</tr>
<tr>
<td>2</td>
<td>Tris(thiourea)zinc sulphate</td>
<td>262.65</td>
<td>*</td>
</tr>
<tr>
<td>3</td>
<td>Lithium niobate</td>
<td>100.00</td>
<td>[30]</td>
</tr>
<tr>
<td>4</td>
<td>L-histidine tetrafluoroborate</td>
<td>116.72</td>
<td>#</td>
</tr>
<tr>
<td>5</td>
<td>L-histidine diphosphate</td>
<td>113.17</td>
<td>#</td>
</tr>
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</table>

* Present work; # Chapter – IV.
6.6 Conclusions

The second order NLO materials ULMA and ZTS were synthesized and the solubility test reveals that water is the best solvent for the growth of single crystals at 30°C. The effect of pH on the morphology of the grown crystal has been studied for ZTS and it shows that the crystal grows larger in (100) and (010) planes. The thermal and microhardness studies indicate that the grown crystals have a good thermal and mechanical stability for optical applications. The materials have a good optical transmittance in the entire visible region with short lower cutoff wavelengths. The optical birefringence was measured by the interference technique as a function of temperature. The powder SHG efficiency of these materials is comparable to KDP and shows the phase matching property. The laser damage threshold of these materials is greater than the well-known NLO material LiNbO₃.
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