Chapter – 5

Growth and Characterization of pure and L-Lysine doped Zinc (Tris) thiourea sulphate crystals
CHAPTER – 5
GROWTH AND CHARACTERIZATION OF PURE AND L-LYSINE DOPED ZINC (TRIS) THIOUREA SULPHATE CRYSTALS

5.1. INTRODUCTION

For the past several years, scientists working on NLO materials were making an intense search for new NLO materials which combine the high optical nonlinearity and chemical flexibility of organics with the high mechanical strength of inorganics [1-3]. In this context, coordination complex [4] were also considered as important NLO materials. The understanding of the nonlinear polarization mechanisms and their relation to the structural characteristics of the materials has been considerably improved. The new development of techniques for the fabrication and growth of artificial materials has dramatically contributed to this evolution. The aim is to develop materials presenting large nonlinearities and satisfying at the same time all the technological requirements for applications such as wide transparency range, fast response, and high damage threshold. But in addition to the processability, adaptability and interfacing with other materials, improvements in nonlinear effects in devices, led the way to the study of new NLO effects and the introduction to new concepts. Zinc tris(thiourea)sulphate (ZTS) is one such organic-inorganic hybrid NLO material with excellent non-linear optical properties ZTS, Zn[CS(NH2)2]3SO4, is a metal-organic nonlinear optical crystal which can be grown fairly easily in large sizes from aqueous solutions.

Its growth and characterization have been reported in a number of publications [5-10]. High damage threshold and wide transparency of ZTS crystal make it a better alternative for KDP crystals for frequency-doubling and laser fusion [11,12]. ZTS is
an efficient semiorganic nonlinear material for type II secondharmonic generation [13-15]. ZTS is nearly 1.2 times more nonlinear than KDP [16] and it has a high damage resistance [17] too.

Amino acids play an important role in the field of nonlinear optical crystals [18,19]. Most of natural amino acids are individually exhibit NLO properties. Amino acids in solution at natural pH are predominantly zwitter ions rather than unionized molecules. The tetrahedral array of four different groups about a carbon atom conforms optical activity on amino acids [20]. Thus, amino acids may be used as dopant in order to enhance the material properties such as NLO. Efforts have been made to improve the ferroelectric properties of the TGS family crystals by doping with various amino acids [21,22]. Recently, Su et al. [23] have reported that the L-lysine doped TGS (Triglycine sulphate) single crystals show improved ferroelectric properties and structural changes. However, the detailed growth aspects and the effect of dopant on the dielectric and mechanical properties have not been studied. Recently, L-lysine doped TGS was proposed as a new IR detector [24,25]. So, we have attempted to grow ZTS crystal by doping it with optically active basic amino acid L-lysine. In this study the effect of L-lysine dopant in changing the crystal morphology, lattice parameter, mechanical and optical properties of ZTS has been reported. For experimental evidences the results of single X-ray analysis, FT-IR, optical transmission, thermal, SHG and microhardness measurements is reported.
5.2. MOLECULAR STRUCTURE

5.2.1. Molecular Structure of L-Lysine

Lysine is an α-amino acid with the chemical formula \( \text{HO}_2 \text{CCH(NH}_2\text{)(CH}_2\text{)}_4 \text{NH}_2 \). It is an essential amino acid, which means that the human body cannot synthesize it. The ε-amino group often participates in hydrogen bonding and acts as a general base in catalysis. (The ε-amino group, which is attached to the \( \text{NH}_3^+ \) group, is the fifth carbon down from the α-carbon, which is attached to the carboxyl (\( \text{C=OOH} \)) group). The molecular structure of L-lysine is shown in Figure 5.1(a).

5.2.2. Molecular Structure of ZTS

Zinc tris(thiourea)sulphate (ZTS) is one of the organic–inorganic hybrid NLO material with excellent non-linear optical properties. It is a metal-organic nonlinear optical crystal. The molecular formula of ZTS is \( \text{Zn}[\text{CS(NH}_2\text{)}_3\text{]}\text{SO}_4 \) (Figure 5.1(b)).

5.2.3. Molecular structure of L-Lysine doped ZTS

By doping optically active basic amino acid L-lysine in pure ZTS, single crystals of L-lysine doped ZTS can be grown. These crystals have orthorhombic structure as shown in Figure 5.1(c).
Figure 5.1(a): Molecular structure of L-Lysine
Figure 5.1(b): Molecular structure of ZTS
Figure 5.1(c): Molecular structure of L-Lysine doped ZTS
5.3. CRYSTAL GROWTH

The ZTS salt was synthesized by dissolving high purity AR grade Zinc sulphate and thiourea in molar ratio 1:3 in de-ionized water. The solution was stirred using magnetic stirrer. Where in white crystalline ZTS salt was obtained. ZTS salt was synthesized [26,27] according to the reaction:

\[ \text{ZnSO}_4 + 3\text{CS(NH}_2\text{)}_2 \rightarrow \text{Zn}[\text{CS(NH}_2\text{)}_2]_3\text{SO}_4 \]

The component salts were well dissolved in de-ionized water and it was thoroughly mixed using a magnetic stirrer and the mixture was heated at 50°C till a white crystalline salt of ZTS was obtained. The temperature was maintained at 50°C to avoid decomposition. To synthesize L-lysine doped ZTS crystals, the parent material (ZTS) was recrystalized and 1 mol % of L-lysine was added to the solution of ZTS separately and the same procedure was also followed as for undoped ZTS crystals. Transparent colorless ZTS crystals of size $14 \times 12 \times 2 \text{ mm}^3$ were harvested in 18 days and L-lysine doped ZTS crystals, of size $11 \times 8 \times 2 \text{ mm}^3$ with good transparency were harvested in 30 days as shown in Figure 5.2(a) and Figure 5.2(b).
Figure 5.2(b): The Photograph of L-Lysine Doped ZTS Crystal
5.4. CHARACTERIZATION STUDIES

The grown crystals have been analyzed by different characterization techniques. The grown single crystals of pure and amino acid doped ZTS were confirmed by single crystal X-ray diffraction analysis using ENRAF NONIUS CAD4 diffractometer. The functional groups were identified by using PERKIN ELMER RXI FT-IR in the range of 400-4000 cm⁻¹. The optical properties of the crystals were examined between 200 and 1200 nm using LAMBDA-35 UV-Vis spectrometer. The NLO efficiency of the grown sample was confirmed using Nd:YAG laser as the source. The mechanical property of the grown crystals have been studied using a Leitz Weitzler hardness tester fitted with a diamond pyramidal indenter. The thermal property of the grown crystals have also been analysed. To obtain the structural perfection and growth features of the grown crystal, etching studies were done.

5.4.1. X-ray Diffraction Analysis

The single crystal X-ray diffraction study has been carried out to confirm the crystallinity and to determine the lattice parameters of the grown sample. The single crystal X-ray diffraction has been carried out using ENRAF NONIUS CAD4 diffractometer. The structure was solved by the direct method using SHELXL program. From the XRD data it is observed that both pure and L-lysine doped crystals are orthorhombic. The calculated lattice parameter values of pure and L-lysine doped ZTS are presented in Table 5.1. The results of the present work are in good agreement with the reported values [28]. In the case of doped sample, a slight variation in the cell volume is observed.
Table 5.1
Single-crystal XRD data of pure and L-lysine doped ZTS crystals

<table>
<thead>
<tr>
<th>Pure ZTS</th>
<th>L-lysine doped ZTS</th>
</tr>
</thead>
<tbody>
<tr>
<td>$a = 7.797\text{ Å}$</td>
<td>$a = 7.789\text{ Å}$</td>
</tr>
<tr>
<td>$b = 11.144\text{ Å}$</td>
<td>$b = 11.150\text{ Å}$</td>
</tr>
<tr>
<td>$c = 15.512\text{ Å}$</td>
<td>$c = 15.517\text{ Å}$</td>
</tr>
<tr>
<td>$\alpha = \beta = \gamma = 90^\circ$</td>
<td>$\alpha = \beta = \gamma = 90^\circ$</td>
</tr>
<tr>
<td>$V = 1348\text{ Å}^3$</td>
<td>$V = 1347.5\text{ Å}^3$</td>
</tr>
<tr>
<td>Orthorhombic</td>
<td>Orthorhombic</td>
</tr>
<tr>
<td>Pca2$_1$</td>
<td>Pca2$_1$</td>
</tr>
</tbody>
</table>
5.4.2. FT-IR Studies

FT-IR spectrum of pure and L-lysine doped ZTS crystal was recorded using the KBr pellet technique in the frequency region 400-4000 cm⁻¹ using PERKIN ELMER RXI FT-IR. The recorded FT-IR spectrum of pure and L-lysine doped ZTS crystal is shown in Figure 5.3. In the FT-IR spectrum of ZTS, the intensity 3195.24 cm⁻¹ is due to N-H stretching vibration of the NH₂ group of thiourea. The C=S stretching vibrations occurs at 1624.44 cm⁻¹. The peaks at 1512.94 and 1368.51 cm⁻¹ are due to HN₂ bending vibration. C-N vibration is a peak at 1122.36 cm⁻¹. The peaks at 712.75 and 471.44 cm⁻¹ are tentatively assigned to Zn-S vibrations because the crystal is devoid of covalently bonded water to Zinc.

In the FT-IR spectrum of L-lysine doped ZTS, the intensity 3187.49 cm⁻¹ is due to N-H stretching vibration of the NH₂ group of thiourea. The C=S stretching vibrations occurs at 1627.55 cm⁻¹. The peaks at 1505 and 1402 cm⁻¹ are due to NH₂ bending vibration. C-N vibration is a peak at 1122.02 cm⁻¹. The peaks at 708.71 and 476.14 cm⁻¹ are tentatively assigned to Zn-S vibrations. So the L-lysine doped ZTS crystal is devoid of covalently bonded water to Zinc. The spectrum of L-lysine doped ZTS displays nearly similar features as that of ZTS. Examinations of the peak position illustrates substantial shifts for the peaks as shown in Table 5.2. This is the clear indication for the presence of amino acid, L-lysine in the lattice of ZTS crystal.
Table 5.2
FT-IR data comparison of pure and L-lysine doped ZTS single crystals

<table>
<thead>
<tr>
<th>Pure ZTS wavenumber (cm⁻¹)</th>
<th>L-lysine doped ZTS wavenumber (cm⁻¹)</th>
<th>ASSIGNMENT</th>
</tr>
</thead>
<tbody>
<tr>
<td>3195.24</td>
<td>3187.49</td>
<td>N-H stretching</td>
</tr>
<tr>
<td>1624.44</td>
<td>1627.55</td>
<td>C=S stretching</td>
</tr>
<tr>
<td>1512.94</td>
<td>1505</td>
<td>NH₂ bending</td>
</tr>
<tr>
<td>1368.51</td>
<td>1402</td>
<td>NH₂ bending</td>
</tr>
<tr>
<td>1122.36</td>
<td>1122.02</td>
<td>C-N vibration</td>
</tr>
<tr>
<td>712.75</td>
<td>708.71</td>
<td>Zn-S vibrations</td>
</tr>
<tr>
<td>471.44</td>
<td>476.14</td>
<td>Zn-S vibrations</td>
</tr>
</tbody>
</table>
Figure 5.3: FT-IR spectra of pure and L-lysine doped ZTS crystal
5.4.3. Optical Studies

The UV-Visible spectrum analysis has been measured using LAMBDA-35 UV-Vis spectrophotometer in the wavelength range of 200-1200 nm. The UV-VIS spectrum gives limited information about the structure of the molecule because the absorption of UV and visible light involves promotion of the electron in $\sigma$ and $\pi$ orbital from the ground state to higher energy states. To find the transmission range of ZTS, the optical transmission spectrum of the ZTS for the wavelengths between 200 and 1200 nm was recorded. The recorded optical transmission spectrum is shown in Figure 5.4. The transmittance is found to be maximum in the entire visible and infrared regions. On consideration of the percentage of transmission observed that for L-lysine doped ZTS crystals, the transmission has increased from 60% to 75% in the visible region. From the spectrum it is observed that the transmittance percentage of doped ZTS crystal is 15% higher than that of the pure grown crystal. The crystal shows a good transmittance in the entire visible region. The lower cutoff at 270 nm for both pure and doped ZTS crystals attest the usefulness of this material for optoelectronic applications and the second harmonic generation of the Nd:YAG laser and for the generation of the higher harmonics of the laser diodes. A good optical transmittance is very desirable in a NLO crystal, since the absorptions, if any, in an NLO material near the fundamental or the second harmonics of an Nd:YAG laser, 1064 nm and 532 nm respectively, will lead to loss of conversion efficiency of SHG.
Figure 5.4: UV-Vis spectra of pure and L-lysine doped ZTS
5.4.4. Thermal Analysis

The thermal analysis (TGA) was carried out by using TAQ-500 analyser at a heating rate of 25°C/min for temperature range of 50 to 900°C in nitrogen inert atmosphere to study the weight loss and thermal stability. The thermograms are shown in Figure 5.5(a) and Figure 5.5(b). It reveals that in the case of L-lysine doped ZTS crystals, the weight loss about 30% takes place in 244.75°C and 302.66°C and for pure ZTS crystals weight loss about 30.62%, takes place at 240.75°C and 304.87°C. There is no weight loss upto 100°C, ensuring the absence of water in the crystal structures. The first weight loss is due to decomposition of both the compounds and the second weight loss is due to organic compound evaporation and liberation of volatile substances like sulphur dioxide [29]. The sharpness of the endothermic peak shows good degree of crystallinity of the grown crystal. In the DTA curve the first endothermic peak has been observed at 244.75°C for L-lysine doped ZTS crystal and at 240.75°C for pure ZTS crystals. The endothermic peaks at 360.66°C for L-lysine doped ZTS and 341.10°C for pure ZTS indicate the beginning of decomposition. The doped crystals are more stable than pure ZTS crystals. Comparing the melting points of pure and doped crystals, it is evident that both the grown crystals are stable upto 240°C and are best suited for NLO applications.
Figure 5.5(a): TG and DTA Thermograms of ZTS Crystals
Figure 5.5(b): TG and DTA Thermograms of L-Lysine Doped ZTS Crystals
5.4.5. SHG Efficiency Measurement

The SHG conversion efficiency of ZTS was measured by Kurtz and Perry powder technique [30]. The grown crystals were subjected to the NLO study to measure the SHG efficiency. The grown crystals were ground into a fine powder and densely packed between two transparent glass slides. A Q switched Nd: YAG laser emitting a fundamental wavelength of 1064 nm, pulse energy 3 mJ/pulse, pulse width 8 ns and repetition rate 10Hz was allowed to strike the sample cell. The emission of green light confirmed the SHG efficiency of pure and doped ZTS crystals. The optical signal generated from the sample was recorded using an oscilloscope. The measured outputs were 28mV and 45mV for pure ZTS and L-lysine doped ZTS crystals. KDP was used as the reference material with SHG efficiency of 21mV. Since both the materials have higher SHG efficiency than KDP (21 mV), they are best suitable for NLO applications.

5.4.6. Microhardness Measurement

The mechanical property of the grown crystals have been studied using a LEITZ microhardness tester fitted with a Vickers diamond pyramidal indenter. A well polished crystal was placed on the platform of Vickers microhardness tester and the loads of different magnitudes were applied over a fixed interval of time. The indentation time was kept (10s) for all the loads. The hardness number was calculated using the relation

\[ H_v = \frac{(1.8544 \times P)}{d^2} \text{ kg/mm}^2 \]

where \( H_v \) is the Vicker's microhardness number, \( P \) is the applied load in kg and \( d \) is the diagonal length of the indentation impression in micrometer. A graph has been
plotted between hardness number (Hv) and applied load (P) as shown in Figure 5.6(a). In both pure and L-lysine doped ZTS crystals, the hardness decreases gradually with the increase of load and at higher concentration of impurity the hardness tends to saturate. The possible explanation for this behavior is as follows. In the solid state, L-lysine exists as Zwitter ions. So, introduction of L-lysine in the crystal lattice of ZTS creates ionic vacancy. All these defects, act as obstacles to dislocation motion, thus decreasing the hardness of the crystals. At higher concentration of impurity, the impurity-vacancy associates into larger aggregate. So, hardness saturates at higher concentration of impurity.

The relation connecting the applied load (P) and diagonal length (d) of the indenter is given by the Meyer’s Law [31]. From Meyer’s Law $P = ad^n$ connecting the applied load (P) and diagonal length (d) of the indentation, the work hardening coefficient ‘n’ was calculated. Here ‘a’ is a constant for a given material. From the observations on various materials [32,33], it is pointed out that ‘n’ lies between 1 and 1.6 for hard materials and is greater than 1.6 for soft materials. From the graph shown in Figure 5.6(b) and Figure 5.6(c), for pure and L-Lysine doped ZTS single crystals, the calculated value of ‘n’ is 1.83 and 1.727 respectively. This suggests that the grown crystals are relatively soft. According to Onitsch [33], n is expected to be less than 2 which has been proved in the grown crystals.
Figure 5.6(a): Plot of Load vs. Hardness of ZTS and L-Lysine doped ZTS crystal
Figure 5.6(b): Log d vs. log p curve for ZTS crystal
Figure 5.6(c): Log d vs. log p curve for L-lysine doped ZTS crystal
5.4.7. Etching Studies

To obtain the structural perfection and growth features of a grown crystal, etching studies can be used. The (100) plane of the pure and doped ZTS crystal was completely immersed for 10s in the water etchant and the sample was wiped out with dry filter paper. Using a Magnus MLX Microscope the features of the crystal has been analyzed which is shown in the Figure 5.7(a) and Figure 5.7(b). From the figures, number of etch pits have been identified with identical shape. By increasing the etching time, the pattern remain the same but the size of the etch pits increases. The etch pits can be attributed to the initial dislocations formed at low angle boundaries or segregated impurities.
Figure 5.7(a): Etch patterns on pure ZTS - 10 sec

Figure 5.7(b): Etch patterns on L-lysine doped ZTS - 10 sec
5.5. CONCLUSION

Good optical quality pure ZTS and L-lysine doped ZTS single crystals have been grown by solution growth method at room temperature. The lattice parameters have been found using single crystal X-ray diffraction technique and confirmed by powder XRD results. The FT-IR spectrum reveals the various functional groups present in the grown crystal. The optical absorption spectrum reveals that the absorbance is less between 300 and 1200 nm. This illustrates the absence of any overtones or combination modes above 270 nm and absorbance due to electronic transition between 300 and 1100 nm. The Vicker’s microhardness was calculated in order to understand the mechanical stability of the grown crystals. Hardness measurement also shows that L-lysine doped crystals are much harder than pure ZTS crystals. Both the crystals are of soft nature. TG and DTA curves show that both the crystals are stable upto 240°C. The studies on the NLO property confirmed the second harmonic conversion efficiency of the crystal to be better than KDP. The crystal perfections and quality have been identified by using the etching studies.
REFERENCES


