CHAPTER 2

GROWTH AND CHARACTERIZATION OF A SEMIORGANIC NONLINEAR OPTICAL CRYSTAL
THIOUREA CADMIUM–ZINC SULPHATE (CZTS)

2.1 INTRODUCTION

Nonlinear optics plays an important role in the emerging era of photonics. Photonics involves the application of photons for information and image processing. Nonlinear optical processes have applications in vital functions such as frequency conversion and optical switching (Prasad and Williams 1991). Organic crystals can have very large nonlinear susceptibilities relative to inorganic crystals, but exhibit low damage threshold and poor processibility (Ledoux et al 1990, Dou et al 1993, Knopfle et al 1995 and Serbutoviez et al 1995). In contrast, pure inorganic NLO materials typically have excellent mechanical and thermal properties, but often possess relatively modest optical nonlinearities due to their lack of extended electron delocalization.

Inorganic crystals grown from high temperature melts may typically have lower laser damage thresholds, and more optical inhomogeneities throughout the bulk, due to impurities and defects resulting from the extremely non-equilibrium growth conditions. In order to retain the merits and overcome the shortcomings, some new classes of NLO crystals such as semiorganic crystals have been developed. Semiorganic crystal is one in which the typically high-optical nonlinearity of a purely organic ion is
combined with the favourable mechanical property and thermal properties of an inorganic counter ion (Kotler et al 1992).

Semi-organic materials possess large nonlinearity, high resistance to laser induced damage, low angular sensitivity and good mechanical hardness compared to organic and inorganic materials (Velsko 1990, Mohankumar et al 2005, Singh et al 1993 and Badan et al 1993). Hence, much attention has been paid to grow new semi-organic nonlinear optical materials, in view of their potential applications in the field of telecommunications, optical information storing devices and second harmonic generation.

The thiourea molecule is an interesting inorganic matrix modifier due to its large dipole moment and ability to form extensive network of hydrogen bonds (Landolt et al 1982). The optical limiting behavior in thiourea metal complexes were discussed (Dhanuskodi et al 2011). Some of the reported promising NLO crystals of thiourea complex are zinc tris thiourea sulfate (Venkataraman et al 1995), potassium thiourea bromide (Roshan et al 2001), bis thiourea cadmium chloride (Selvakumar et al 2005), zinc thiourea chloride (Rajasekaran et al 2001) and bis thiourea zinc chloride (Angelimary and Dhanuskodi 2001).

Zinc tris (thiourea) sulfate is a desirable semi-organic nonlinear optical material, which exhibits low angular sensitivity, and is useful for type-II second-harmonic generation (Marcy et al 1992, Ushasree et al 1999). A study on the nucleation kinetics of tris thiourea zinc cadmium sulphate was reported (Jayalakshmi and Kumar 2006). The thermal and mechanical properties of tris thiourea zinc cadmium sulphate was studied (Jayalakshmi and Kumar 2008).
This chapter reports the synthesis and the growth of a semiorganic nonlinear optical crystal thiourea cadmium-zinc sulphate (CZTS) by the slow evaporation technique. The grown crystals have been subjected to single crystal X-ray diffraction (XRD), Powder X-ray diffraction, Fourier transform infrared (FTIR) spectroscopy, optical absorption, thermal, dielectric, micro hardness, morphology, etching and second harmonic generation (SHG) efficiency studies.

2.2 EXPERIMENTAL

2.2.1 Synthesis

Thiourea cadmium-zinc sulphate (CZTS) was synthesized from cadmium sulphate, zinc sulphate and thiourea taken in the stoichiometric ratio of 1:1:3 as per the following reaction

\[ \text{Zn SO}_4 + \text{Cd SO}_4 + 3\text{NH}_2\text{CSNH}_2 \rightarrow \text{ZnCd (NH}_2\text{CSNH}_2)_3(\text{SO}_4)_2 \]

The purity of the synthesized salt was increased by a successive re-crystallization process.

2.2.2 Solubility

The solubility and its temperature dependence are essential for aqueous solution growth. Solubility data will be adequate to start growing good quality crystals. The solubility of the synthesized material has been determined at four different temperatures 303 K, 308 K, 313 K, 328 K. The solubility was determined by dissolving the solute in de-ionized water in an air-tight container maintained at a constant temperature with continuous stirring. After attaining saturation, the equilibrium concentration of the solute was analyzed gravimetrically in steps of 5 K from 303 K to 318 K. The
solubility of CZTS as a function of temperature is shown in Figure 2.1. It has been observed that the material has moderate solubility.

![Solubility curve of thiourea cadmium-zinc Sulphate (CZTS)](image)

Figure 2.1 Solubility curve of thiourea cadmium-zinc Sulphate (CZTS)

### 2.2.3 Crystal Growth

The growth rate of a crystal plane is dependent on a set of parameters like temperature, the degree of super saturation of the solution, pH, impurities concentration and other physio-chemical properties (Arunmozhi et al 1997). In general, the following equation can be used to express the functional relation \( R = F(T, S, \text{pH}, C) \), where \( R \) expresses the growth rate of the crystal, \( T \), \( S \) and \( C \) express, respectively, the temperature, super saturation and concentration of the impurity in the solution.
Figure 2.2 Single crystal of thiourea cadmium-zinc sulphate

The required amount of synthesized salt, as per the solubility data was added slowly to double distilled water. The solution was stirred well using a magnetic stirrer for 1 h to ensure homogeneous temperature and concentration over the entire volume of the solution. Then the solution of pH 3.0 was filtered using 0.1 micron porosity filter paper and transferred to a petri dish. Crystallization was allowed to take place by slow evaporation under room temperature. Care was taken to minimize thermal variations and mechanical disturbances. The photograph of the as-grown single crystal of CZTS is shown in Figure 2.2.

2.3 RESULTS AND DISCUSSION

2.3.1 X-ray Diffraction studies

Single-crystal X-ray Diffraction is a non-destructive analytical technique which provides detailed information about the internal lattice of crystalline substances.

Single crystal X-ray diffraction studies of CZTS were carried out using the ENRAF NONIUS CAD4 diffractometer. From the studies, it was
found that the crystal belongs to the triclinic system with the space group P1. The cell parameters are $a = 8.7385\ \text{Å}, \ b = 9.0547\ \text{Å}, \ c = 9.7478\ \text{Å}$, $\alpha = 91.755^\circ, \ \beta = 110.641^\circ, \ \gamma = 95.472^\circ Z = 2$ and volume $V = 771.12\ \text{Å}^3$.

A Powder X-ray diffraction of CZTS has been carried out using a Siemens Rich-Seifert diffractometer with CuK$\alpha$ ($\lambda = 1.5418\ \text{Å}$) radiation. The sample was scanned over the range 10°–60° at a rate of 1°/min. The powder X-ray diffraction pattern is shown in Figure 2.3. The X-ray diffraction peaks were indexed for the lattice parameters and the prominent peaks obtained from powder X-ray diffraction confirm the crystalline property of the grown crystals.

![Figure 2.3 Powder X-ray diffraction pattern of CZTS](image)

2.3.2 UV-Vis-NIR Spectral Analysis

The optical properties of crystalline materials give information regarding the composition, nature, and quality of the crystal. Absorption
spectra are very important for any NLO material because, an NLO material can be of practical use only if it has a wide transparency window. Figure 2.4 shows the optical absorption spectrum of a single CZTS crystal. The lower cut off wavelength is observed at 380 nm. From the spectrum it is seen, that the crystal is found to be transparent in the region of 400–1200 nm which is an essential parameter for the frequency doubling process.

![Figure 2.4 UV-Vis-NIR absorption spectrum of CZTS](image)

2.3.3 FTIR Spectral Analysis

The preferred method of infrared spectroscopy is the FTIR. When infrared radiation (IR) is passed through a sample, some amount of radiation is absorbed and the remaining is transmitted. The molecules of the sample absorb IR if the frequency of the radiation matches the vibrational frequency
of the molecule. The resulting spectrum represents the molecular absorption and transmission, creating a molecular fingerprint of the sample.

The FTIR analysis (Silversitein et al 1998) of the CZTS crystal was carried out using a BRUKER IFS 66V model spectrophotometer by KBr pellet method in the wave-number range of 4000 to 450 cm\(^{-1}\) as shown in Figure 2.5.

![FTIR Spectrum of CZTS](image)

**Figure 2.5  FTIR Spectrum of CZTS**

Crystal structure investigations of thiourea have established the coplanarity structure of the C, N and S atoms in the molecules (Andreeti et al 1968). In the CZTS complex, two possibilities by which the coordination of cadmium with thiourea can occur. The coordination of cadmium may occur either through nitrogen or sulfur of thiourea. The functional groups present in the spectrum are given in Table 2.1.
Table 2.1 Frequency assignments for CZTS crystal

<table>
<thead>
<tr>
<th>Band</th>
<th>Mode</th>
<th>Wave number (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>N-H</td>
<td>Symmetric stretching</td>
<td>3393,3286</td>
</tr>
<tr>
<td>O-H</td>
<td>Symmetric stretching</td>
<td>3202</td>
</tr>
<tr>
<td>C-H</td>
<td>Symmetric stretching</td>
<td>2694</td>
</tr>
<tr>
<td>N-H</td>
<td>Bending</td>
<td>1613</td>
</tr>
<tr>
<td>C-S</td>
<td>Symmetric stretching</td>
<td>1437,1409</td>
</tr>
<tr>
<td>C-O</td>
<td>Symmetric stretching</td>
<td>1123,1032</td>
</tr>
<tr>
<td>=C-H</td>
<td>Bending</td>
<td>968</td>
</tr>
<tr>
<td>N-H</td>
<td>Wagging</td>
<td>713</td>
</tr>
<tr>
<td>C-H</td>
<td>Bending</td>
<td>619</td>
</tr>
<tr>
<td>C-S</td>
<td>Symmetric stretching</td>
<td>525</td>
</tr>
</tbody>
</table>

The absorption bands at 3393 cm\(^{-1}\) and 3286 cm\(^{-1}\) correspond to N-H symmetric stretching vibration. The O-H symmetric stretching vibration appears at 3202 cm\(^{-1}\). The peak at 2694 cm\(^{-1}\) is assigned to the C-H symmetric stretching vibration. The N-H bending vibration is observed at 1613 cm\(^{-1}\). The C-S symmetric stretching vibrations are assigned at 1437 cm\(^{-1}\) and 1409 cm\(^{-1}\) respectively. The peaks at 1123 cm\(^{-1}\) and 1032 cm\(^{-1}\) are assigned to the C-O symmetric stretching frequency. The =C-H bending vibration appears at 968 cm\(^{-1}\). The peak at 713 cm\(^{-1}\) is due to the N-H wagging vibration. The C-H symmetric stretching vibration is observed at 619 cm\(^{-1}\). The C-S symmetric stretching vibration appears at 525 cm\(^{-1}\). Thus the functional groups in the FTIR spectrum confirm the formation of the CZTS crystal.
2.3.4 Thermal Analysis

Thermal analysis comprises of the Differential thermal analysis (DTA) and the Thermogravimetric analysis (TGA). The chemical reaction, phase transformation, and structural changes that occur in a sample during heating or cooling can be studied by the DTA. The TGA is performed on samples to determine changes in weight in relation to transition, thermal degradation, and chemical reaction.

The thermal behavior of the CZTS was analyzed using the ZETZSCH-Geratebau GmbH thermal analyzer. The sample was heated in nitrogen atmosphere in an aluminium crucible in the temperature range of 473 K to 1073 K at a heating rate of 10 K/min. The TGA and DTA thermograms are shown in Figure 2.6 (a) and 2.6 (b).

![TGA thermogram of CZTS](image-url)
Figure 2.6 (b) DTA thermogram of CZTS

A sharp weight loss observed at 363 K, is attributed to the loss of lattice water. This is followed by two more stages one at 483 K and the other at 664.1 K. The total weight loss of these states amounts to 73%. The resulting residue gives a weight loss for a wider range of temperatures between 673 K and 1073 K, which is found to be 27%. Since the total weight loss corresponds to 100% it clearly indicates that no residue remains. The sharp endothermic peaks in the DTA trace nearly coincide with decompositions shown in the TGA trace. Though the decomposition point of the material is 483K, the compound loses its crystal structure at 363 K itself due to the loss of lattice water. Hence, the compound can be utilized for nonlinear optical applications below 363 K.

2.3.5 Dielectric Studies

The capacitance and conductivity of a material is defined by its dielectric properties. A single crystal of thiourea cadmium-zinc sulphate was
subjected to dielectric studies. The variation of the dielectric constant against frequency at room temperature for the crystal is shown in Figure 2.7 (a).

![Graph showing variation of dielectric constant with frequency of CZTS](image)

**Figure 2.7(a) Variation of dielectric constant with frequency of CZTS**

In general, the dielectric constant is higher at the lower frequencies and then decreases with increasing frequency, and remains constant at a higher frequency region. The dielectric constant of CZTS crystal is found to be high. The large values of the dielectric constant at low frequency, suggest that there is a contribution from all four known sources of polarization, namely, electronic, ionic, dipolar, and space charge polarization. Further, the space charge polarization will depend on the purity and perfection of the material. When the electric charge carriers cannot follow the alternation of the ac electric field applied beyond a certain critical frequency, the dielectric constant decreases with increasing frequency and remains constant.
The variation of the dielectric loss with frequency is shown in Figure 2.7(b). The characteristic of the low dielectric loss with high frequency suggests that the sample possesses enhanced optical quality with lesser defects (Balarew and Duhlew 1984).

Figure 2.7(b)  Variation of dielectric loss with frequency of CZTS

2.3.6  Morphology and Facets

Morphology has been developed to predict the external morphology of a crystalline material from its internal crystal structure. The relationship between the crystal morphology and the internal arrangement of atoms in the crystal is therefore of great interest to chemists, chemical engineers, and process engineers. Morphology allows researchers to study the crystal shape
and to consider the effects of altering the growth rate of particular faces on crystal morphology.

![Figure 2.8 Single crystal morphology of CZTS](image-url)

Figure 2.8 Single crystal morphology of CZTS

The morphology of a thiourea cadmium-zinc sulphate crystal was determined by contact goniometry and is depicted in Figure 2.8. The prominent planes are (111), (203), (231), (010), (010) and (001). The (001) plane is the most prominent plane and the other well-developed planes (010), and (010) dominates the crystal morphology. The morphology studies indicates that the CZTS crystal grows faster along the [100] direction.
2.3.7 Vickers Microhardness Test

One of the important properties of any device material is its mechanical strength, represented by its hardness. Physically, hardness is the resistance offered by a material to localized plastic deformation (Mott 1956) caused by scratching or indentation. This resistance is the intrinsic property of the crystal. The hardness is generally measured as the ratio of the applied load to the surface area of the indentation. The hardness index can also be correlated with other mechanical properties such as elastic constants (Wooster 1953) and yield strength.

The microhardness measurement for the grown crystal was made using a Richert – MD 4000E Ultra micro-hardness tester fitted with a Vicker’s diamond pyramidal indentor attached to an incident light microscope. A grown crystal with a smooth and dominant face (001) was selected for microhardness studies. In ideal circumstances, the measured hardness values should be independent of the applied load. But in practice, load dependence is observed. The static indentations were made at room temperature with a constant indentation time of 3 seconds. The indentation marks were made on the surfaces by varying the load from 25 g to 100 g. The Vickers microhardness number $H_v$ of the crystal was calculated using the relation $H_v = 1.8544 \frac{P}{d^2} \text{ MPa}$. A graph plotted between the hardness number ($H_v$) and the applied load ($P$) is shown in Figure 2.9 (a).
Figure 2.9 (a) Hardness behaviour of CZTS

It is observed from the graph, that the hardness value increases with an increase in the applied load. Above 90 g, the hardness suddenly decreases, as cracks developed in the material. This may be due to the release of internal stresses generated locally by indentation.

A plot between Log (P) against Log (d) shown in Figure 2.9 (b) gives a straight line which is derived from the Meyer’s law, the relation connecting the applied load is given by P= ad^n. Here ‘n’ is the Meyer index or strain hardening co-efficient, ‘d’ is the mean diagonal length of the indenter impression, and ‘a’ is an arbitrary constant for a given material. The value of ‘n’ should be between 1 and 1.6 for the harder material and above 1.6 for the softer material. The strain hardening co-efficient of the crystal calculated from the slope of Log (P) versus Log (d) was found to be 2, which establishes CZTS as a soft material.
2.3.8 Etching Studies

Growth feature and etch pits reveal reciprocity (Shitole and Saraf 2002). Chemical etching is one of the simple and powerful methods to analyze the defects present in the growing crystal surfaces. The presence of dislocation in crystals is inferred from the etch pits observation (Sangwal 1987). Dislocations easily appear in crystals, especially in the initial stages of their growth (Chernov 1989). Once the damaged surface layer was removed by means of etching, a fresh surface appeared, which in turn gave clear etch pits. The etching of the CZTS crystal was carried out by using deionized water as an etchant at room temperature for an etching time of 10, 20 and 30 s.
The surface features of the crystal before etching are shown in Figure 2.10(a). The surface is not smooth before etching. No particular pattern of growth is visible. Traces of rectangular etch pits are seen for an etching time of 10 s as indicated in Figure 2.10(b). When the crystal is etched for another 10 s, well defined rectangular etch pits are observed, as shown in Figure 2.10(c). Figure 2.10(d) represents elongated rectangular patterns for a time of 30 s. The observed etch pits, due to layer growth, confirmed the two-dimensional nucleation mechanism with less dislocations (Mukerji and Kar 1999).

Figure 2.10 Etchpit patterns observed on CZTS single crystal with water as an etchant (a) before etching (b) 10 s (c) 20 s and (d) 30 s
2.3.9 Second Harmonic Generation Test

The powder SHG test (Kurtz and Perry 1968) enables one to measure the optical nonlinearity (NLO) efficiency of new materials relative to standard urea or KDP. Also it is possible to confirm the existence of the phase matching property in new materials.

A Q-switched Nd:YAG laser of energy 2.0mJ/pulse at 1064 nm with a repetition rate of 10 Hz and pulse width of 9ns was used as a fundamental source of light. The input laser beam was passed through an IR reflector and then directed on the microcrystalline powdered sample packed in a capillary tube of diameter 0.154 mm. The power of the incident beam was measured using a power meter. The transmitted fundamental wave was passed over a monochromator, which separates 532 nm (SHG signal) from 1064 nm and is absorbed by a CuSO₄ solution. The green light was detected by a photomultiplier tube and displayed on a storage oscilloscope. The KDP was used as a reference material and the SHG relative efficiency of the thiourea cadmium-zinc sulphate crystal was found to be 1.8 times higher than that of KDP. The comparison of the NLO efficiency of CZTS with similar materials Cadmium Zinc Thiourea acetate and Cobalt Thiourea Sulphate with respect to the KDP are listed in Table 2.2.

Table 2.2 Comparison of NLO efficiency of CZTS with other organic materials with respect to KDP

<table>
<thead>
<tr>
<th>Name of the compound</th>
<th>NLO Efficiency</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thiourea cadmium-zinc sulphate (Title compound)</td>
<td>1.8</td>
</tr>
<tr>
<td>Cadmium Zinc Thiourea acetate (Kirubavathi et al 2008)</td>
<td>0.22</td>
</tr>
<tr>
<td>Cobalt Thiourea Sulphate (Kirubavathi et al 2007)</td>
<td>0.18</td>
</tr>
</tbody>
</table>
2.4 CONCLUSION

Semi-organic nonlinear optical crystal thiourea cadmium-zinc sulphate (CZTS) has been grown by the slow evaporation solution growth technique. The solubility studies were performed at various temperatures. Single crystal X-ray diffraction studies reveal that CZTS belongs to the triclinic system. The crystallinity of the compound is confirmed by powder X-ray diffraction and the diffraction peaks were indexed for the lattice parameters $a = 8.7385 \ \text{Å}, \quad b = 9.0547 \ \text{Å}, \quad c = 9.7478 \ \text{Å}$. The UV-Vis-NIR absorption spectrum shows high transmittance from the cut off wavelength 380 nm to 1200 nm. The functional groups present in the compound were analyzed by the FT-IR spectrum, which confirms the formation of the CZTS. The DTA and the TGA analyses reveal that the melting point of the crystal is 363 K. The dielectric constant and dielectric loss studies of the crystal establish its normal behaviour. Morphology studies indicate that the (001) plane is the most prominent one among the other developed planes. From the hardness measurement, it is found that the crystal is mechanically stable up to 90 g. Etching studies reveals that the crystal grows by the two dimensional layer growth mechanism. The SHG relative efficiency of the thiourea cadmium-zinc sulphate crystal was found to be 1.8 times higher than that of KDP.