CHAPTER 2

GROWTH AND CHARACTERIZATION OF PURE CADMIUM THIOUREA ACETATE SINGLE CRYSTALS

2.1 INTRODUCTION

In the recent years an intense worldwide effort has been focused on the research of design and development of materials with large optical nonlinearity. Also, photonics is playing an ever increasing role in our modern information society (Paresh 2004). Interests have been centered on semiorganic crystals which have the combined properties of both inorganic and organic crystals like high laser damage threshold, wide transparency range, less deliquescent and nonlinear coefficients which make them suitable for device fabrication. Metal organic complexes offer higher environmental stability combined with greater diversity of tunable electronic properties by virtue of the co-ordinated metal center.

Compounds belonging to urea analogs were incorporated into inorganic salts and their NLO properties were widely studied in recent experiments (Sastry 1999). The nonlinear optical (NLO) properties of some complexes of thiourea have attracted significant attention in the last few years because both organic and inorganic components contribute specifically to the process of second harmonic generation (Bhat and Dharmaprakash 1997). Thiourea molecule, which is centrosymmetric, yields excellent noncentrosymmetric materials (Venkataramanan et al 1997). The thiourea molecule is an interesting inorganic matrix modifier due to its large dipole
moment (Landolt Bornstein 1982) and its ability to form an extensive network of hydrogen bonds. Among the semiorganic nonlinear optical materials, metal complexes of thiourea which have low UV cut off wavelengths, applicable for high power frequency conversion are of interest. Also thiourea molecule co-ordinates with several metal ions to form stable co-ordinate complexes, which can be crystallized either by solution growth technique or by gel growth technique. Some of the potential thiourea complexes are zinc thiourea sulphate, bis thiourea cadmium chloride (Ushashree et al 1999, 2000), zinc thiourea chloride (Rajasekaran et al 2001) and copper thiourea chloride. These crystals have better nonlinear optical property than KDP. Cadmium thiourea acetate (CTA) is one among the various thiourea complexes.

Attempts were made to grow crystals of CTA (Rajesh et al 2004) and the nucleation kinetics of this crystal was carried out by Sankar et al (2006). However, thorough searches on literature revealed the need of a detailed analysis on the growth and characterization of CTA. In the present investigation, the experiments were performed to grow CTA crystals by slow evaporation solution growth technique. Characterization studies such as powder XRD and HRXRD were carried out. The theoretical factor group analysis was carried out for the prediction of the various vibrational modes. The Raman and infrared spectra were recorded to study the structure and functional groups of the material. Etching studies were carried out to analyse the nature of dislocations on the crystal. With an insight to learn the properties of the material, dielectric and photoconductivity studies were carried out on the sample.
2.2 GROWTH OF CADMIUM THIOUREA ACETATE SINGLE CRYSTALS

2.2.1 Material Synthesis

Cadmium thiourea acetate (CTA) was synthesized by mixing cadmium acetate and thiourea in the ratio 1:2 in deionized water. The reaction mechanism is as follows

$\text{(CH}_3\text{COO)}_2\text{CdH}_2\text{O} + 2 \text{CH}_4\text{N}_2\text{S} \rightarrow \text{C}_6\text{H}_{14}\text{CdN}_4\text{O}_4\text{S}_2 + \text{H}_2\text{O}$

The mixtures of the reactants were stirred well to avoid co-precipitation of multiple phases since thiourea has the co-ordination capacity to form different phases of metal-thiourea complexes. The product obtained was purified by repeated recrystallisation before it was used for crystal growth.

2.2.2 Solubility

Crystals grow in a variety of shapes in response to both internal and external factors. Some of these factors can be manipulated (e.g., solvent type, solution temperature and supersaturation) by crystal growers/materials scientists to steer crystal towards a target shape or away from undesired shapes (Klug 1993). To grow bulk crystals, it is always desired to select a solvent in which it is moderately soluble.

The solubility of CTA in ethanol and water was determined for four different temperatures. The salt of CTA was dissolved in deionized water in an air tight container maintained at a constant temperature with constant stirring. After attaining saturation, the equilibrium concentration of the solute was determined gravimetrically. The procedure was repeated for the other
temperatures. The similar procedure has been repeated using ethanol as solvent. The solubility as a function of temperature is shown in Figure 2.1. From the solubility graph, it is observed that as temperature increases the concentration of the solute also increases for both the solvents. The figure indicates that the solubility is good in deionized water.

![Figure 2.1 Solubility curve of CTA](image)

### 2.2.3 Crystal Growth

The obtained salt of CTA was purified by repeated recrystallization in deionized water before growth. The resultant CTA was dissolved in deionized water and heated above its saturation temperature. The solute was added till the supersaturation was attained and then the solution was gradually cooled to crystallize to get the seed crystal. Crystals of CTA were grown from aqueous solution by slow evaporation solution growth technique. 200 ml of the solution was saturated at 35°C and then filtered to remove any insoluble
impurities. The seed obtained from slow evaporation was employed for the growth. The growth experiments were performed in a constant temperature bath at 35°C. Good quality single crystals were obtained in a period of 5-20 days. The obtained crystals are non-hygroscopic and free from inclusions. The grown CTA crystal is shown in Figure 2.2.

Figure 2.2 As grown CTA crystal

2.3 STRUCTURAL CHARACTERIZATION OF CTA CRYSTALS

2.3.1 Powder X-ray Diffraction Studies

The powder X-ray diffraction pattern was recorded for CTA using a Rich Seifert X-ray diffractometer with CuKα (λ= 1.5418 Å) radiation over the range of 10° to 70° at a scanned rate of 1°/min and is shown in Figure 2.3. The peaks were indexed by using the Proszi software package. It is confirmed that CTA crystallizes in the orthorhombic crystal system with the P2_12_12 space group. The packing of CTA is in such a way that in each unit
cell there are four molecules. The calculated lattice parameters are \( a = 7.56 \, \text{Å}, \)
\( b = 11.86 \, \text{Å}, \) \( c = 15.68 \, \text{Å}, \) \( \alpha = \beta = \gamma = 90^\circ \) and the cell volume \( V = 1405.89 \, \text{Å}^3. \)
The present experimental values are in good agreement with the reported literature (Rajesh et al 2004).

![Powder X-ray diffraction pattern of CTA](image)

**Figure 2.3** Powder X-ray diffraction pattern of CTA

### 2.3.2 High Resolution X-Ray Diffraction Studies on CTA Crystal

Good quality single crystals are much needed for device fabrication. The defects are discrete entities and their location and degree of disturbance produced in a lattice can be determined experimentally. The high resolution X-ray diffraction technique is a non-destructive analysis and can be used for direct observation of boundaries and dislocations (Kato 1975 and Tanner 1976).
To reveal the crystalline perfection of the specimen crystals, a multicrystal X-ray diffractometer (MCD) designed and developed at National Physical Laboratory, New Delhi (Lal and Bhagavannarayana1989), has been used to record high resolution diffraction curves (DCs). The schematic representation of this system is shown in Figure 2.4. In this system a fine focus (0.4 mm × 8 mm; 2 kW Mo) X-ray source energized by a well-stabilized Philips X-ray generator (PW 1743) was employed. The well-collimated and monochromated MoKα₁ beam obtained from the three monochromator Si crystals set in dispersive (+,−,−) configuration has been used as the exploring X-ray beam. The specimen crystal is aligned in the (+,−,−,+) configuration. Due to dispersive configuration, though the lattice constants of the monochromator crystal(s) and the specimen are different, the unwanted dispersion broadening in the diffraction curve of the specimen crystal is insignificant.

Before recording the diffraction curve, the specimen surface was prepared by lapping and polishing and then chemically etched by a non-preferential chemical etching using the etchant of the mixture of water and acetone in 1:2 ratio. Figure 2.5 shows the high resolution X-ray diffraction curve (rocking curve) recorded with multicrystal X-ray diffractometer using (111) diffracting planes for CTA single crystal. The solid line (convoluted curve) is well fitted with the experimental points represented by the open circles. On de-convolution of the diffraction curve, it is found that the curve contains an additional peak, which is 68 arc sec away from the main peak. The additional peak corresponds to an internal structural low angle boundary (tilt angle ≥ 1 arc min but less than a deg) whose tilt angle (mis-orientation angle between the two crystalline regions on both sides of the structural low angle boundary) is 68 arc sec. The full width at half maximum (FWHM) of the main peak and the low angle boundary are respectively
43 and 159 arc sec. Though the specimen contains low angle boundary, the relatively low angular spread of around 400 arc sec of the diffraction curve shows that the crystalline perfection of CTA crystal is reasonably good. The segregation of impurities or the entrapment of solvent molecules at the boundaries could be responsible for the observed very low angle boundary. It may be mentioned here that such low angle boundaries could be detected with well resolved peaks in the diffraction curve only because of the high resolution of the multicrystal X-ray diffractometer used in the present study.

Figure 2.4  Schematic of multicrystal X-ray diffractometer
2.3.3 Photoluminescence Studies

To detect the lower concentration of defects the photoluminescence (PL) studies are preferred rather than optical absorption. This is a mechanism where the impurity on absorption of light gives rise to bound excited state from which it returns to its ground state abiding in the analysis of colour centre creation mechanism. The room temperature PL spectrum of CTA is shown in Figure 2.6. When the excitation wavelength is 488 nm, two peaks are observed at 540 nm and 600 nm. The emission at 540 nm indicates the presence of intrinsic defects in the forbidden band region for this CTA crystal (Meijerink et al 1990). This can be also inferred from the HRXRD studies which show the presence of defects or very low angle boundary.
Figure 2.6 Photoluminescence spectrum of CTA

The origin of green band can be attributed to the relaxation of polarization defects formed by the strained sites attached to oxygen vacancies. Oxygen vacancy is a common defect in metal doped crystals which induce distortion of the lattice in its direct surrounding (Schulman 1963). Further this green emission band at 540 nm may be assigned to the transitions between filled $\pi$ to anti – bonding $\pi^*$ orbital of the metal ligand (Yasushi Aoki et al 1996). The peak appearing at 600 nm is also attributed to the presence of the intrinsic defects in the forbidden band region, as the spectral range of the peak occurring at 66 nm is in the greenish yellow band revealing the characteristic colour of CTA crystals. The presence of minute defects in substantied with the HRXRD studies.

2.3.4 Spectral Analyses
2.3.4.1 Factor group analysis

The factor group and the site group are important in the application of group theoretical methods for the analysis of spectra of solids. An
additional advantage of the factor group method is that it provides a basis for the prediction of the infrared and Raman spectra of lattice vibrations.

CTA crystallizes in the orthorhombic crystal system with the noncentrosymmetric space group $P2_12_12_1$ ($D_2^4$). The factor group analysis of the unit cell of CTA is carried out using the character table for the point group $C_i(4)$, which is isomorphic with the factor group. The 4 molecules of the primitive unit cell of CTA occupy general sites of $C_i(4)$ symmetry. A single molecule of CTA contains 31 atoms which in turn gives rise to $(31 \times 4)$ 124 atoms in a unit cell. Group theoretical analysis of the fundamental modes of CTA crystal reveal that there are 369 vibrational optical modes and are seen to decompose into $\sum_{369} = 93A + 92B_1 + 92B_2 + 92B_3$ along with three acoustic modes ($B_1 + B_2 + B_3$). The procedure outlined by Rousseau et al (1981) was followed to carry out the factor group analysis of the title compound. The results are presented in Table 2.1. Polarizability tensors associated with orthorhombic crystals like CTA are of the form

$$A = \begin{bmatrix} \alpha_{xx} & 0 & 0 \\ 0 & \alpha_{yy} & 0 \\ 0 & 0 & \alpha_{zz} \end{bmatrix}$$

$$B_1(Z) = \begin{bmatrix} 0 & \alpha_{xy} & 0 \\ \alpha_{yx} & 0 & 0 \\ 0 & 0 & 0 \end{bmatrix}$$

$$B_2(Z) = \begin{bmatrix} 0 & 0 & \alpha_{xz} \\ 0 & 0 & 0 \\ \alpha_{zx} & 0 & 0 \end{bmatrix}$$

$$B_3(Z) = \begin{bmatrix} 0 & 0 & 0 \\ 0 & 0 & \alpha_{yz} \\ 0 & \alpha_{zy} & 0 \end{bmatrix}$$

The polarizability tensors are depicted along the crystallographic X, Y and Z axes. Phonons belonging to $B_1$, $B_2$ and $B_3$ are both Raman and infrared active. However the phonons belonging to A symmetry are Raman active and infrared inactive. The summary of the factor group analysis of CTA is presented in Table 2.2.
Table 2.1 Results of factor group analysis of CTA

<table>
<thead>
<tr>
<th>S No</th>
<th>Factor group Symmetry ( (D_4^2) )</th>
<th>A</th>
<th>B₁</th>
<th>B₂</th>
<th>B₃</th>
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<tr>
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<td>(i) Translational</td>
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<td>3</td>
<td>3</td>
<td>3</td>
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<tr>
<td></td>
<td>(ii) Rotational</td>
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<td>3</td>
<td>3</td>
<td>3</td>
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<td>2</td>
<td>Internal Modes</td>
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<td>87</td>
<td>87</td>
<td>87</td>
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<tr>
<td></td>
<td>Total</td>
<td>93</td>
<td>93</td>
<td>93</td>
<td>93</td>
</tr>
</tbody>
</table>

Table 2.2 Factor group analysis – summary

<table>
<thead>
<tr>
<th>Factor group symmetry ( (D_4^2) )</th>
<th>Site symmetry</th>
<th>Ext</th>
<th>Int</th>
<th>C</th>
<th>H</th>
<th>Cd</th>
<th>N</th>
<th>O</th>
<th>S</th>
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<th>Acoustic modes</th>
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<tr>
<td>A</td>
<td>3T,3R</td>
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<td>18</td>
<td>42</td>
<td>3</td>
<td>12</td>
<td>12</td>
<td>6</td>
<td>93</td>
<td>0</td>
<td></td>
</tr>
<tr>
<td>B₁</td>
<td>3T,3R</td>
<td>87</td>
<td>18</td>
<td>42</td>
<td>3</td>
<td>12</td>
<td>12</td>
<td>6</td>
<td>93</td>
<td>1</td>
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<tr>
<td>B₂</td>
<td>3T,3R</td>
<td>87</td>
<td>18</td>
<td>42</td>
<td>3</td>
<td>12</td>
<td>12</td>
<td>6</td>
<td>93</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>B₃</td>
<td>3T,3R</td>
<td>87</td>
<td>18</td>
<td>42</td>
<td>3</td>
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<td>12</td>
<td>48</td>
<td>48</td>
<td>24</td>
<td>372</td>
<td>3</td>
<td></td>
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</tr>
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</table>
2.3.4.1.1 Vibrational analysis of CTA

Analysis on the vibrational spectra reveals the information regarding the nature of bonding, structures of co-ordination compounds and material confirmation.

The molecular structure of CTA enumerates that the title compound consists of NH$_2$, N-C-N, C=S, COO$^-$ groups etc. The observed / calculated vibrations of CTA could be due to lattice vibrations and internal vibrations of these groups. The formal classification of fundamental mode reveals 348 internal vibrations which can be attributed as $(87A + 87B_1 + 87B_2 + 87B_3)$ and 24 external modes contributed by 12 translational $(3A + 3B_1 + 3B_2 + 3B_3)$ and 12 librational $(3A + 3B_1 + 3B_2 + 3B_3)$ modes.

The bands observed between 3300 and 350 cm$^{-1}$ in Figures 2.7 and 2.8 arise from the internal modes of CTA. The bands obtained below 350 cm$^{-1}$ arise from the deformational vibrations and the librational and translational modes of anions and cations. Table 2.3 presents the correlation scheme obtained by following the procedures of Fateley et al (1972). Each internal mode of CTA ions should split into four components of which $B_1(X)$, $B_2(Y)$ and $B_3(Z)$ are infrared active and all $A$ (XX, YY, ZZ), $B_1$(XY), $B_2$(XZ) and $B_3$(YZ) are Raman active.
Table 2.3 Correlation scheme for CTA

<table>
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<tr>
<th>Site Symmetry C_1</th>
<th>Factor Group Symmetry</th>
<th>Activity</th>
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<tr>
<td></td>
<td>A</td>
<td>α_xx, α_yy, α_zz</td>
</tr>
<tr>
<td></td>
<td>B_1</td>
<td>α_yz</td>
</tr>
<tr>
<td></td>
<td>B_2</td>
<td>α_xz</td>
</tr>
<tr>
<td></td>
<td>B_3</td>
<td>α_yz</td>
</tr>
</tbody>
</table>

2.3.4.1.2 Internal Vibrations

As the CTA molecule does not have any symmetry the internal vibrations exhibited are of both infrared and Raman active exclusive of acoustic mode. The internal vibrations of CTA may be classified as those arising from the NH\textsubscript{2}, N-C-N, C=S, COO\textsuperscript{-} functional groups. These vibrations are strongly coupled between themselves.

2.3.4.1.3 External Vibrations

The bands observed below 300 cm\textsuperscript{-1} are mainly due to external modes, the rotational and translational modes of the ions. The rotational modes are expected to have higher frequency and intensity than translational modes in the Raman spectra. However, the translational modes are more intense in FT-IR spectra (Bhattacharjee 1990 and Hanuza and Fomitsev 1980). In the present investigation CTA is expected to have 45 modes in
Raman at low frequency range corresponding to external modes. They are distributed as \((6A + 5 B_1 + 5 B_2 + 5 B_3)\) translational and \((6A + 6B_1 + 6B_2 + 6 B_3)\) rotational modes. These vibrations can be achieved experimentally by polarized Raman measurements.

### 2.3.5 Infra Red and Raman Spectral Analyses

Infrared spectroscopy finds application in determining the site of co-ordination, the nature of the metal–ligand bonding as well as for the elucidation of structures of co-ordination compounds. The FT-IR spectrum was recorded on Bruker 1FS - 66 V spectrophotometer in the regions 4000–500 cm\(^{-1}\), by KBr pellet method.

Raman spectroscopy is extensively used for obtaining information about various modes in crystals. The FT-Raman spectrum of CTA was recorded using a Bruker IFS – 66V model interferometer equipped with FRA: 106 FT-Raman accessory in the region 3500-50 cm\(^{-1}\) in the Stoke’s region using the 1064 nm line of an Nd : YAG laser for excitation operating at 200 mW power with a resolution ±1 cm\(^{-1}\). The FT-IR and FT-Raman spectra of CTA crystal are shown in Figures 2.7 and 2.8 respectively and the vibrational band assignments are summarized in Table 2.4.
Figure 2.7 FT-IR spectrum of CTA

Figure 2.8 FT-Raman spectrum of CTA
Table 2.4 IR and Raman bands of CTA and their assignments

<table>
<thead>
<tr>
<th>FT-IR (cm(^{-1}))</th>
<th>Raman (cm(^{-1}))</th>
<th>Assignments</th>
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<tr>
<td>3431</td>
<td>-</td>
<td>N – H stretching</td>
</tr>
<tr>
<td>3306</td>
<td>3314</td>
<td>NH(_2) deformation</td>
</tr>
<tr>
<td>-</td>
<td>3228</td>
<td>NH(_2) stretching</td>
</tr>
<tr>
<td>-</td>
<td>2932</td>
<td>C - H stretching</td>
</tr>
<tr>
<td>2767</td>
<td>-</td>
<td>C - H stretching</td>
</tr>
<tr>
<td>-</td>
<td>2430</td>
<td>C - H stretching</td>
</tr>
<tr>
<td>2388</td>
<td>-</td>
<td>C - C stretching</td>
</tr>
<tr>
<td>1956</td>
<td>-</td>
<td>Overtones and Combinations</td>
</tr>
<tr>
<td>1667</td>
<td>1676</td>
<td>C = O stretching</td>
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<td>1629</td>
<td>1636</td>
<td>NH(_2) bending</td>
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<tr>
<td>1495</td>
<td>1508</td>
<td>COO stretching</td>
</tr>
<tr>
<td>1442</td>
<td>1441</td>
<td>C = S stretching</td>
</tr>
<tr>
<td>1346</td>
<td>1363</td>
<td>CH(_2) wagging</td>
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<tr>
<td>1111</td>
<td>1124</td>
<td>N – C - N stretching</td>
</tr>
<tr>
<td>1050</td>
<td>-</td>
<td>C - N stretching</td>
</tr>
<tr>
<td>1018</td>
<td>-</td>
<td>N - H twisting</td>
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<tr>
<td>943</td>
<td>954</td>
<td>C – H deformation</td>
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<td>789</td>
<td>-</td>
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<td>725</td>
<td>733</td>
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<tr>
<td>672</td>
<td>682</td>
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<td>621</td>
<td>633</td>
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<tr>
<td>-</td>
<td>232</td>
<td>Cd – S stretching</td>
</tr>
<tr>
<td>-</td>
<td>117</td>
<td>S – Cd – S bending</td>
</tr>
</tbody>
</table>
Crystal structure investigations of thiourea have established the co-planarity structure of C, N and S atoms in the molecules (Andreeti et al 1968). The symmetric and asymmetric stretching modes of NH₂ grouping of cadmium co-ordinated thiourea is positioned between 2750 and 3500 cm⁻¹. The spectrum shows that bands of thiourea were not shifted to lower frequencies on the formation of CTA complex which indicates that bonding between nitrogen and cadmium is not present in the co-ordination compounds. The absorption band found at 1629 cm⁻¹ in the spectrum of CTA can be assigned to the NH₂ bending vibration. The absorption observed at 1495 and 1111 cm⁻¹ in the spectrum of CTA corresponds to the absorption bands at 1470 and 910 cm⁻¹ of thiourea and can be assigned to the N-C-N stretching vibration. The increase in the frequency can be attributed to the greater double bond character of the carbon to nitrogen bond on complex formation. The absorption band at 1442 cm⁻¹ can be assigned to the C=S stretching vibration.

The presence of sulphate ion in the co-ordination sphere is clearly evident by its peaks around 500 and 1000 cm⁻¹. It is of interest to note that a low frequency band near 730 cm⁻¹ has been assigned to C=S stretching in thiourea. It shifts to lower frequencies by 30-40 cm⁻¹ in co-ordination to a metal. This shift is observed at a frequency of 725 cm⁻¹. Thus the C=S group in thiourea has predominantly a single bond character due to strong mesomeric effect of the adjacent nitrogen atoms. The C-N stretching frequency of thiourea has been found to increase on co-ordination. The low frequency band in the region of 700-900 cm⁻¹ is assigned to coupled C=S stretching modes. There is no evidence for co-ordination of thiourea through nitrogen since it involves significant loss of delocalization energy.

The low frequency vibrations are more active in the Raman spectra. The stretching mode of Cd is identified at 232 cm⁻¹. The lattice vibrations of
thiourea based complexes usually appear in the region 10-300 cm\(^{-1}\). The strongest peak observed at 117 cm\(^{-1}\) is due to lattice vibrations of thiourea and Cd co-ordinated tetrahedral bonds (Krishnakumar and Nagalakshmi 2005).

### 2.4 ETCHING STUDIES OF CTA

Crystals of better perfection are of demand for the use in the electronic devices. The etching studies reveal the structural perfection and growth features of grown single crystals. The geometry of the etch pits formed on different faces of a crystal is related to the crystal structure. The shape of each pit is useful to obtain information about the anisotropic character of faces. Etching techniques are commonly used for the study of the mobility of the dislocations in the crystal.

The chemical etching studies were carried out on the as grown single crystals of CTA to study the symmetry of the crystal from the shape of etch pits and the distribution of structural defects in the grown crystals (Sangwal 1987). Etching was carried out at room temperature (36\(^\circ\)C) for a known duration ranging from 5 seconds to 30 seconds using water as the etchant. The etched surfaces were dried by gently pressing between two filter papers and the surface micro-morphology was photographed under an optical microscope (Leitz Wetzler) in reflected light.

The surface morphology of the as grown single crystal is shown in Figure 2.9a. Figure 2.9b shows the etch pattern obtained after chemical etching of the surface of the crystal for 5 seconds. On observing the image one could identify the growth spirals. It is often found that growth spirals of monomolecular step height are not observed on the crystal; instead spirals with step heights of the order of several times the height of monomolecular step are observed. A spiral corresponds to a group of dislocations, each having a unit Burgers vector, and the visible layers originating from screw
dislocations. Moreover it is found that the chemical etching yielded a number of triangular shaped micro pits in the crystal. A micro pit revealing such a symmetric shape as a triangle should have resulted from the internal structural symmetry of the crystal. On increasing the etching time from 5s to 15s the chemical etching described above has additionally caused a number of etch hillocks (Figures 2.9c-d) and also the etch pits became prominent and well defined etch patterns were obtained. Further increasing the time to 30s increases the number of well defined patterns. Also it is well noted that on increasing the etching time the pits enlarge whilst retain their general shape.

Figure 2.9  (a) As grown surface of CTA crystal (b), (c) & (d) etched surfaces of CTA by water for 5 sec, 15 sec and 30 sec respectively (magnification 160 X)
Thus the etch figures especially the micro pits of symmetrical shapes are related to the internal structural symmetries and probably originate from the existing structural defects. Also the growth spirals may be due to the formation of the crystal at low supersaturation.

2.5 DIELECTRIC STUDIES OF CTA CRYSTAL

Dielectric properties are correlated with the electro-optic property of the crystals (Boomadevi and Dhanasekaran 2004). The dielectric constant of the sample was measured using HIOKI 3532 50 LCR meter. Good quality crystals were selected for the dielectric studies. The samples were polished on a soft tissue paper with fine grade alumina powder (0.1µm) and water as lubricant. High degree of flatness and parallelism was achieved. Each sample was electroded on either side with air drying silver paste so that it behaved like a parallel plate capacitor. The studies were carried out from room temperature to 368 K for the frequencies varying from 50 Hz to 5 MHz. A small cylindrical furnace (20 cm × 20 cm × 20 cm), whose temperature was controlled by Eurotherm temperature controller (± 0.1°C) was used to house the sample.

The frequency dependence of the dielectric constant at different temperature is shown in Figure 2.10. The dielectric constant decreases with increasing frequency and becomes almost saturated beyond 10 kHz for all temperatures. The high value of dielectric constant is attributed to high ionic conductivity. Most of the solid electrolytes have high dielectric constant (Sudharsan et al 1985). The magnitude of dielectric constant depends on the degree of polarization and charge displacement in the crystals. The dielectric constant of materials is due to the contribution of electronic, ionic, dipolar and space charge polarizations which depends on the frequencies (Dharmaprakash and Mohan Rao 1989). At low frequencies all these polarizations are active.
The space charge polarization is generally active at lower frequencies and high temperatures.

It is well known that the capacitance and dielectric constant of a material are in proportion to each other and hence the dependence of capacitance on frequency is similar as in Figure 2.10. From the figure it is observed that capacitance decreases with increasing frequency and becomes almost constant beyond 10 kHz. This effect can be attributed to the effect of charge distribution by mean carrier hopping on the defects. At low frequencies, the charge on the defects can be rapidly redistributed so that defects closer to the positive side of the applied field become negatively charged, while defects closer to the negative side of the applied field become positively charged. This leads to a screening of the field and an overall reduction in the electric field. As capacitance is inversely proportional to the field, this reduction in the field for a given voltage results in the increased capacitance observed when the frequency is lowered. However, at high frequency the defects no longer have enough time to rearrange in response to the applied voltage, and so the capacitance decreases (Zukowski et al 1989 and Vasudevan et al 1998).

The variation of dielectric loss (\(\tan \delta\)) with frequency is shown in Figure 2.11. It is well observed that the dielectric loss decreases with increasing frequency. The low value of dielectric loss indicates that the grown crystals are of moderately good quality (Benet Charles and Gnanam 1994). The larger values of dielectric loss (\(\tan \delta\)) at lower frequencies may be attributed to space charge polarization owing to charged lattice defects (Smyth 1965). From Figure 2.12 it is inferred that the thermal activation on charge carriers is negligible ie., the variation of dielectric constant with varying temperature is very meager or negligible which suggests that the
sample possesses high chemical homogeneity (Hiremath and Venkataraman 2003).

Figure 2.13 shows the frequency dependence of the ac conductivity in the frequency range $10^1$ to $10^7$ Hz in the temperature interval 35°C to 95°C. It is observed that the conductivity increases with increasing frequency. The ac conductivity shows a typical behaviour; a power law increase at frequencies between $10^5$ to $10^7$ Hz. This frequency dependence of the ac conductivity is given by the power law (Gudmundsson et al 2003);

$$\sigma_{ac}(\omega) = a \omega^s$$

(2.1)

where $a$ and $s$ are constants. The frequency dependent exponent $s$ is a characteristic parameter representing the many body interactions of the electrons, charges and impurities (Angadi et al 2003). It depends on the material temperature and is generally less than or equal to unity (Gudmundsson et al 2003); for ideal Debye type samples it is equal to unity. The power law dependence of the frequency is of a universal nature and corresponds to the short ranges that are separated by energy barriers of varied heights. This regime is attributed to hopping conduction (Angadi et al 2003) which sets in frequency above $10^4$ Hz and the regime is clearly visible for the sample.
Figure 2.10  Variation of dielectric constant with frequency of CTA

Figure 2.11  Variation of tan δ with frequency of CTA
Figure 2.12 Variation of dielectric constant with temperature of CTA

Figure 2.13 Variation of conductivity with frequency of CTA
2.6 PHOTOCONDUCTIVITY STUDIES OF CTA CRYSTAL

Polished sample of CTA in rectangular dimensions was fixed on a glass plate. Electrical contacts were made on the sample by silver painted copper wire as electrode with an electrode distance of 0.064 cm. The sample was then connected in series to a DC power supply and a picoammeter (Keithely-480). The applied electric field to the sample was increased from 5 to 140 V/cm without exposing the sample to any radiation and the corresponding dark current (I_d) was recorded. The sample was then illuminated with the radiation from a halogen lamp (100 W) and the photocurrent (I_p) due to the generation of carriers by photoexcitation was recorded for the same range of applied fields.

Figure 2.14 shows the plot of dark current (I_d) and photocurrent (I_p) as a function of applied field. The dark current (I_d) and the photocurrent (I_p) show linear response to the applied field. Also, it is found that at any instant the dark current is greater than the photocurrent and hence it is concluded that CTA single crystal exhibits negative photoconductivity. The studies of Pathinettam Padiyan et al (2000) indicate that the loss of water molecules can also lead to the decrease in the conductivity. However this cannot be true in the case of CTA as the crystal does not contain water molecule in its structure. The negative photoconductivity exhibited by the sample may be due to the reduction in the number of charge carriers or their life time in the presence of radiation (Bube 1981). The decrease in lifetime with illumination could be due to the trapping process and increase in carrier velocity is given by the relation

\[ \tau = (vsN)^{-1} \]  \hspace{1cm} (2.2)
where \( v \) is the thermal velocity of the carriers, \( s \) is the capture cross section of the recombination centers and \( N \) is the carrier concentration. As intense light falls on the sample, the lifetime decreases (Ashraf et al 2004). Stockmann model explains the tendency of decrease in mobile charge carriers during negative photoconductivity. According to this model, for the CTA crystal the negative photoconductivity is based on the state between the Fermi level and the valence band (Pandi and Jayaraman 2001). This state has high capture cross sections for electron and holes. Also this state can capture electrons from the conduction band and holes from the valence band. Thus, the net number of mobile charge carriers is reduced due to incident radiation, giving rise to negative photoconductivity (Joshi 1990).

![Figure 2.14](image.png)

Figure 2.14  Plot of photocurrent / dark current as a function of applied field for CTA
The absorbance spectrum of the grown CTA crystal was recorded by using a Varian Cary 5E UV-VIS-NIR spectrometer in the wavelength range 200 nm–800 nm. The variation of absorbance with wavelength is shown in Figure 2.15. It is to be noted that the absorbance is found to be minimum in the entire visible region. However around 225 nm there is a sharp decrease in transmittance due to absorbance leading to electronic excitation in this region. This is the key requirement of NLO. The lack in distortion observed in the absorbance spectrum indicates the good quality of the crystal.

Figure 2.15 Absorbance spectrum of CTA crystal
2.8 TGA-DTA ANALYSES OF CTA

The thermal behaviour of CTA was analyzed between 25°C and 350°C in the nitrogen atmosphere at a heating rate of 5°C/min using a STA 409°C analyzer. The recorded spectra is shown in Figure 2.16. The TGA results reveal that there is a total weight loss of 56.21% at 320°C. Also it is noted from figure that CTA exhibits only single stage of decomposition and hence decomposes directly without producing any weight loss dependent intermediate species. From the trace it is clear that there are no free non co-ordinated thiourea in this sample.

Figure 2.16 TGA-DTA of CTA crystal
2.9 MICROHARDNESS TEST

The fastest and simplest type of mechanical testing is the hardness measurement. Mechanical properties of the materials such as toughness, brittleness, yield strength, etc., have specific correlation with hardness. Also the structure and composition of the crystalline solids are inviolably related to the mechanical hardness. The hardness of a material is defined as the resistance it offers to the motion of dislocations, deformation, or damage under an applied stress. Among the different testing methods, the Vicker’s hardness test is most commonly used.

The hardness measurements were made on the smooth face (111) of the crystal in room temperature using Leitz – Wetzler Vicker’s hardness tester fitted with a Vicker’s diamond pyramidal indenter and attached to an incident light microscope (Neophot – 2 of Carl – Zeiss, Germany). Loads ranging from 1 g to 15 g in steps of 2 g where hardness is found to be a function of indenter load were used for making indentations, keeping the time of indentation constant at 10 s for all the cases. The two diagonals of the indentation left in the surface of the crystal after removal of the load were measured using a micrometer eyepiece and their average length was calculated. The microhardness $H_v$ was computed using the relation

$$H_v = 1.8544 \left( \frac{P}{d^2} \right) \text{ kg / mm}^2$$

(2.3)

where $P$ is the applied load in kg and $d$ is the average diagonal length in millimeters.

Loads up to 15g were used for the hardness measurement, since the development of cracks does not seem to influence the deformation mechanism.
as long as the impression remains reasonably well defined and the crack does not extend considerably compared with the impression diagonal. Figure 2.17a depicts the variation of hardness with the applied load. Generally the variation of load with hardness number depends on any of the following criteria

(i) hardness decreases with increasing load
(ii) hardness increases with increasing load
(iii) hardness remains constant with increasing load

In the present studies it is quiet interesting to observe the reverse indentation size effect where the microhardness increases with increasing load. The mechanical stress applied by the indenter generates dislocations at the region of the indentation. Thus the major contribution to the increase in hardness with the load is attributed to the high stress required for homogeneous nucleation of dislocations in the small dislocation free region intended. The Vicker’s hardness number for CTA crystal at 15g indenter load is 22.5 kg mm$^{-2}$.

The variation of crack length with load is shown in Figure 2.17b. It is observed that as load increases the crack length increases. This is due to the deeper penetration of the indenter resulting in breakage or loosening of the bond. Further, during the initial stage the surface stress resists the crystal from breaking. On increasing the load this stress state becomes weaker. This can be inferred from the quality of the crystal and the growth pattern studies made using HRXRD and etching.

Fracture toughness is the property of the material that deals with the resistance of the crystal, when subjected to higher loads. The two types of crack systems namely radial-medial and Palmqvist can be formed in a material as a result of indentation (Ponton and Rawlings 1989). At a well
defined value of C/a, ‘C’ being the crack length measured from the center of the indentation mark to the crack end and ‘a’ being half the diagonal length of the indentation mark, transition occurs from palmqvist to radial-median cracks. For C/a ≤ 2.5, the cracks developed are palmqvist.

In CTA crystals the type of crack observed is palmqvist. The fracture toughness $K_c$ for median type crack is calculated using the relation

$$K_c = \frac{k_p^{1/2}}{(a l^{1/2})} \ g / \mu \text{m}^{3/2} \quad (2.4)$$

where the constant $k = 1/7$ for the Vicker’s indenter and $l = c-a$ is the mean Palmqvist crack length. From Figure 2.17c it is inferred that fracture toughness is higher for CTA crystals. Hence CTA is a reasonably harder material.

The brittleness of a material is an important property that determines the mechanical nature of a material. It gives an insight about the fracture induced in a material without any appreciable deformation. The value of brittleness index, $B_i$ is calculated using the relation

$$B_i = \frac{H_v}{K_c} \ m^{-1/2} \quad (2.5)$$

The variation of brittleness with load is depicted in Figure 2.17d. Figures 2.17c and 2.17d very clearly indicate that the increase in hardness is accompanied by increase in toughness and brittleness index.
Figure 2.17a  Variation of hardness number with load for CTA

Figure 2.17b  Crack length with load
Figure 2.17c  Fracture toughness with load

Figure 2.17d  Britleness index with load
Theoretical Calculations of First Order Hyperpolarizability (\(\beta\)) of CTA

The first order hyperpolarizability value of Cadmium thiourea acetate (CTA) was calculated by using the GAUSSIAN 98 W and the computational details used for the calculation of \(\beta\) is already described in section 1.7. The first order hyperpolarizability was calculated using the Equation (1.12). All the calculations were carried out by the Density Functional triply parameter hybrid model DFT/B3LYP using GAUSSIAN 98W. The HF/3-21G (d, p) basis set has been employed. The calculated first order hyperpolarizability of CTA is 5.52E-30 esu. This value is nearly 3 times that of KDP. The calculated first order hyperpolarizability (\(\beta\)) is presented in Table 2.5.

Domination of particular components indicates a substantial delocalization of charges in those directions. The biggest value of hyperpolarizability is noticed in \(\beta_{xy}\) direction and subsequently delocalization of electron cloud is more in that direction. The higher dipole moment values are associated with even larger projection of \(\beta_{total}\) quantities. The electric dipoles may enhance, oppose or at least bring the dipoles out of the required net alignment necessary for NLO properties such as \(\beta_{total}\) values. As S bond in thiourea plays a major role in the molecular hyperpolarizability, the increase of first order hyperpolarizability is originated by the strong hydrogen bond in the thiourea; it leads to a stronger electron delocalization. The enhancement of \(\beta\) is due to the thiourea attached to the cadmium and acetate molecules. It can be noticed that there is small discrepancy in the experimental SHG efficiency value (0.5 times that of KDP) and theoretical hyperpolarizability value (nearly three times that of KDP) which can be due to the strong hydrogen bond formation and the C-N-S which aids in the strong intermolecular bonding.
Table 2.5  First order hyperpolarizability (β) of CTA

<table>
<thead>
<tr>
<th>$\beta_{xxx}$</th>
<th>-254.14</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\beta_{xxy}$</td>
<td>38.33</td>
</tr>
<tr>
<td>$\beta_{xyy}$</td>
<td>-49.71</td>
</tr>
<tr>
<td>$\beta_{yyy}$</td>
<td>15.97</td>
</tr>
<tr>
<td>$\beta_{zxx}$</td>
<td>-109.93</td>
</tr>
<tr>
<td>$\beta_{xyz}$</td>
<td>22.70</td>
</tr>
<tr>
<td>$\beta_{zxy}$</td>
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</tr>
<tr>
<td>$\beta_{xzz}$</td>
<td>-97.10</td>
</tr>
<tr>
<td>$\beta_{yzz}$</td>
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</tr>
<tr>
<td>$\beta_{zzz}$</td>
<td>-95.78</td>
</tr>
<tr>
<td>$\beta_{\text{total}}$</td>
<td>5.52E-30 esu</td>
</tr>
</tbody>
</table>

$\beta(-2\omega;\omega,\omega)$ in $10^{-30}$ esu

2.11  SHG CONVERSION EFFICIENCY OF CTA

Kurtz-Perry powder SHG test remains an extremely valuable tool for initial screening of NLO materials (Kurtz and Perry 1968). A quantitative measurement of the SHG output of CTA crystal was determined by the above technique. The powdered CTA crystal was densely packed between two transparent glass slides. The average size of the finely ground powder particle is much less than the coherent length (~2 µm) for the second harmonic generation. The schematic of the setup used in the present study is shown in Figure 2.18. A Q-switched Nd-YAG (DCR 11) laser was used as a light source. The fundamental laser beam of 1064 nm wavelength, 8 ns pulse width with 10 Hz pulse rate was made to fall normally on the sample cell.
The incident beam power was measured using a power meter. A bright green flash of emission was observed from the CTA sample which indicates the second harmonic generation of the material. The green light was detected by a photomultiplier tube (Hamamatsu R5109, a visible PMT) and displayed on a storage oscilloscope (TDS 3052 B 500 MHz, Phosphor digital oscilloscope). In order to compare the second harmonic generation efficiency, sample of KDP crystal powdered to the identical size was used as a reference material. The experimental result show that the SHG efficiency of CTA is 0.5 times of KDP for a input power of 6.9 mJ/pulse.

![Figure 2.18 Schematic of powder SHG setup](image)

**Figure 2.18 Schematic of powder SHG setup**

### 2.12 CONCLUSION

The co-ordination complex compound cadmium thiourea acetate was synthesized and grown as single crystals by slow evaporation solution
growth method. The HRXRD studies reveal that though the specimen contains low angle boundary, the relatively low angular spread of around 400 arc sec of the diffraction curve shows that the crystalline perfection of CTA crystal is reasonably good. The segregation of impurities or the entrapment of solvent molecules at the boundaries could be responsible for the observed very low angle boundary. The etch pits especially the micro pits of symmetrical shapes are related to the internal structural symmetries and probably originate from the existing structural defects. The theoretical factor group analysis of CTA predicts 369 total vibrational optical modes that decompose into $\Gamma_{369} = 93A + 92B_1 + 92B_2 + 92B_3$ along with three acoustic modes ($B_1 + B_2 + B_3$).

The dielectric studies on the crystal reveal that dielectric constant decreases with increasing frequency but attains saturation for frequencies larger than 10 kHz. The frequency dependent conductivity measurement supports hopping mechanism. Photoconductivity study on the material confirms the negative photoconductivity nature of the crystal. The low transmittance value shows the suitability of the material for NLO application. The calculated first order hyperpolarizability of CTA is 5.52E-30 esu, which is nearly 3 times that of KDP. The enhancement of $\beta$ is due to the thiourea attached to the cadmium and acetate molecules. The variation in the theoretical and experimental values of SHG can be due to the strong hydrogen bond formation and the C-N-S which aids in the strong intermolecular bonding.