CHAPTER – 4

STUDIES ON THE GROWTH AND CHARACTERIZATION OF TETRA (THIOUREA) POTASSIUM CHLORIDE (TTPC) – A SEMIORGANIC NLO MATERIAL

4.1 INTRODUCTION

Second Order Nonlinear optical (SONLO) materials have a significant impact on laser technology, optical communication, optical storage technology and electro optic modulation. The search for new frequency conversion materials over the past decade has led to the discovery of many semi organic materials. These materials posses large non linearity, high resistance laser induced damage and low angular sensitivity [1-3]. The common wisdom has been that an optical material should have a large charge transfer and the optical transparency with less dislocation density [4]. Organic materials show their properties prominently due to their fast and large nonlinear response over a broad frequency range, inherent synthetic flexibility, and large optical damage threshold. However, organic materials suffer from problems, such as volatility, low thermal stability, mechanical weakness, etc. Inorganic materials possess excellent mechanical and chemical properties but most of them show low nonlinear efficiency. The need for materials which combine large nonlinear optical characteristics with resistance to physical and chemical attack led to the investigation of semi-organics [5-8]. Semi-organic materials have the potential for combining high optical nonlinearity and chemical flexibility of organics with the physical ruggedness
of inorganic substances. The advantages of semi-organic materials are that they can be grown from aqueous solution and form large three-dimensional crystals. The crystals can be easily cut and polished with specific phase-matching loci, acceptance angle, and the effective nonlinear coefficient, for frequency doubling of 1064 nm. Ligands like thiourea and thiocyanate with S and N donors are capable of combining with metal to form stable complexes through coordinated bonds. These complexes show ligand to metal charge transfer (LMCT) by an electron movement from ligand to metal and metal to ligand (MLCT) in addition to $\pi - \pi^*$ conjugation. Metals with $d_{10}$ configuration like zinc, cadmium, mercury readily combine with thiourea resulting in stable compounds with high optical nonlinearity and good physiochemical behavior.

In the recent past different types of semiorganic single crystals have been grown by researchers [9-11]. Recently the metal complexes of thiourea are being explored. Some of the examples of these complexes are Zinc Thiourea Chloride (ZTC), Bisthiourea Cadmium Chloride (BTCC) and Copper Thiourea Chloride (CTC). These crystals have better nonlinear optical properties than KDP.

In this chapter, we have successfully grown the compound mentioned in the title by taking appropriate ratio of thiourea and potassium chloride. It is a potential semiorganic nonlinear optical material having a molecular formula $C_4H_{16}Cl KN_8S_4$. It was grown by slow evaporation solution growth technique at room temperature. The grown single crystals have been analyzed by adopting different characterization techniques. The results are elaborated in the forthcoming sections.
4.2 MATERIAL SYNTHESIS AND GROWTH OF TTPC

The recrystallized material of TTPC was synthesized by taking thiourea (AR grade) and potassium chloride (AR grade) in the ratio of 4:1 using water as the solvent. The solution was stirred continuously for 24 hours and subsequently heated to get the homogeneous mixture. Then the saturated solution was allowed to cool to room temperature and kept in a vibration free area with a tightly closed plastic cover for controlled evaporation. TTPC was synthesized according to the following reaction mechanism:

\[ \text{KCl} + 4\text{[CS (NH}_2\text{)_2]} \rightarrow \text{K [CS (NH}_2\text{)_2]}_4\text{Cl} \]

4.3 PURIFICATION OF SYNTHESIZED SALT

Impurities in synthesized salt are of considerable importance, not only because of their influence on the physical and chemical properties of the resulting crystals, but also since they play a dominant role in controlling crystal growth behaviour.

The synthesized salts have more additives and it is essential to remove the precipitates, which are formed during the synthesis. The synthesized material of TTPC was purified by repeated recrystallization processes using water as the solvent. The material was taken in a beaker and water was added until the material was completely dissolved. Then it was subjected to filtration using borosil filter paper having 0.1 porosity microns. Then the solution was subjected to evaporation and the substance was crystallized. Such filtration and recrystallization was done for five times.
4.4 SOLUBILITY

Solubility studies have been carried out using recrystallized salt of TTPC in water. The solubility was determined by 100 ml of solvent was taken in an airtight container and recrystallized salt was added. The experiment was carried out in a constant temperature bath with a cryostat facility. The bath was set to 35 °C and the solution was stirred continuously for five hours with motorized stirrer by ensuring homogeneous temperature and concentration throughout the volume of the solution. The solution was further stirred for five hours after attaining the saturation and the equilibrium concentration of the solute was analyzed gravimetrically. The experiment was carried out at different temperatures, and the solubility curve drawn. The solubility of TTPC in water is shown in Figure 4.1.
Figure 4.1 Solubility curve of TTPC
4.5 CRYSTAL GROWTH

The solvent evaporation technique was employed for the growth of TTPC crystal at room temperature. According to the solubility data the saturated solution of TTPC was obtained by dissolving the recrystallized material with continuous stirring of the solution using magnetic stirrer. The saturated solution was further purified by filtering through the glass filter paper provided with fine pores of size 1 micrometer porosity. The filtered solution was tightly closed with thick filter paper so that the evaporation could be minimized. The solution was kept in an undisturbed condition. Good quality single crystals of tetra (thiourea) potassium chloride (TTPC) have been collected from the mother solution in a time span of 20 days with dimension 14 x 12 x 2 mm$^3$. The grown single crystal is shown in Figure 4.2

4.6 CHARACTERIZATION

The grown crystals have been analyzed by various characterization techniques. The grown single crystal of TTPC was confirmed by single crystal X-ray diffraction analysis using ENRAF NONIUS CAD4 diffractometer. The functional groups were identified by using PERKIN ELMER RX1 Fourier Transform Infrared spectrophotometer in the range of 400-4000 cm$^{-1}$. The optical properties of the crystals were examined between 200 and 1200 nm using SHIMADZU UV-1061 UV-Visible spectrophotometer. The NLO efficiency of the grown sample was confirmed Nd:YAG laser as the source. The mechanical property of the grown crystals has been studied using a Leitz Weitzler hardness tester fitted with a diamond pyramidal indentor. The thermal behaviour of the grown single crystal was tested by Perkin-Elmer thermal analyzer (STA 409 PC).
Figure 4.2 As-grown crystal of TTPC
4.7 RESULTS AND DISCUSSIONS

4.7.1 Single crystal X-ray diffraction analysis

The single X-ray diffraction study was carried out to determine the crystal system and the lattice dimensions of the grown crystal. The grown crystals of TTPC were subjected to single crystal X-ray diffraction studies using an ENRAF NONIUS CAD-4 X-ray Diffractometer with MoKα radiation (\( \lambda = 0.7107 \, \text{Å} \)) to obtain the unit cell dimensions. The cell dimensions were evaluated using standard software. From this measurement we found that the grown specimen belongs to tetragonal system with the lattice parameters \( a = 20.48 \, \text{Å}, \, b = 20.64 \, \text{Å}, \, c = 8.52 \, \text{Å}, \) and \( V = 3578.90 \, \text{Å}^3 \). The results are given in Table 4.1.

<table>
<thead>
<tr>
<th>Identification code</th>
<th>TTPC</th>
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<tbody>
<tr>
<td><strong>Cell parameters</strong></td>
<td></td>
</tr>
<tr>
<td>a = 20.48 Å</td>
<td></td>
</tr>
<tr>
<td>b = 20.64 Å</td>
<td></td>
</tr>
<tr>
<td>c = 8.52 Å</td>
<td></td>
</tr>
<tr>
<td>( \alpha = 90^\circ )</td>
<td></td>
</tr>
<tr>
<td>( \beta = 90^\circ )</td>
<td></td>
</tr>
<tr>
<td>( \gamma = 90^\circ )</td>
<td></td>
</tr>
<tr>
<td><strong>Volume</strong></td>
<td>3578.90 Å³</td>
</tr>
<tr>
<td><strong>System</strong></td>
<td>Tetragonal</td>
</tr>
<tr>
<td><strong>Chemical formula</strong></td>
<td>( \text{C}_4\text{H}_6\text{ClKN}_8\text{S}_4 )</td>
</tr>
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</table>
4.7.2 Fourier Transform Infra-red (FTIR) analysis

The FTIR spectrum of TTPC crystal was in the KBr pellet technique in the frequency region 400-4000 cm$^{-1}$ using PERKIN ELMER RX1 Fourier Transform Infrared spectrometer. The recorded FTIR spectrum of TTPC crystal is shown in Figure 4.3. The observed bands along with their vibrational assignment are summarized and compared with thiourea in Table 4.2. The asymmetric and symmetric NH$_2$ stretching vibrational bands were observed at 3261 and 3162 cm$^{-1}$, respectively. The CH symmetric stretching vibration was observed a sharp peak at 2681 cm$^{-1}$. The NH$_2$ bending vibration appears at 1587 cm$^{-1}$. The CN asymmetric and symmetric stretching vibrations were observed at 1464 and 1089 cm$^{-1}$, respectively. The strong bands appearing at 1427 and 729 cm$^{-1}$ in the spectrum were assigned to CS asymmetric and symmetric stretching vibration. To confirm the metal coordination of thiourea either through S or N, the CN and CS stretching of complex TTPC were compared with free ligand (thiourea). It was established that the CN stretching vibration of thiourea (1089 and 1472 cm$^{-1}$) were shifted to a higher wavenumber of TTPC (1089 and 1464 cm$^{-1}$) and the CS stretching vibrations of thiourea (740 and 1417 cm$^{-1}$) were shifted to a lower wavenumber of TTPC (729 and 1427 cm$^{-1}$). This clearly indicates the coordination of sulfur with metal.
Figure 4.3 FTIR spectrum of TTPC
<table>
<thead>
<tr>
<th>Wavenumber (cm⁻¹)</th>
<th>Assignment</th>
</tr>
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<tbody>
<tr>
<td>Thiourea</td>
<td>TTPC</td>
</tr>
<tr>
<td>3280</td>
<td>3261</td>
</tr>
<tr>
<td>3167</td>
<td>3162</td>
</tr>
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<td>2681</td>
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<tr>
<td>648</td>
<td>626</td>
</tr>
<tr>
<td>469</td>
<td>490</td>
</tr>
</tbody>
</table>

\(\gamma\) – stretching, \(\delta\) – bending, \(\text{as}\) – asymmetric, \(\text{s}\) – symmetric

Table 4.2 Comparisons of IR Band Frequencies (cm⁻¹) Thiourea and TTPC
4.7.3 Thermal analysis

The thermo gravimetric analysis of TTPC crystal were carried out between 20 °C and 800 °C in the nitrogen atmosphere at a heating rate of 20 °C min⁻¹ using Perkin-Elmer thermal analyzer (STA 409 PC). The obtained spectrum is shown in Figure 4.4. From the TG/DTA spectrum, we observed that the weight loss below 245 °C was due to weakly entrapped lattice water and above it, due to the removal of strongly entrapped lattice water. This was followed by a major weight loss at 550 °C due to decomposition of the substance. The DTA analysis was also carried out in the same atmospheric condition. There was an endothermic transition between 180 and 260 °C which was good in agreement with the TGA trace. The sharp endothermic peak at around 186 °C was assigned to the melting point of the title compound. Sharpness of the endothermic peak observed in DTA showed good degree of crystallinity of the specimen [12]. Hence it might be useful for making the NLO devices below its melting point.

4.7.4 Differential scanning calorimetric analysis

Differential scanning calorimeter (DSC) study was performed using DSC 200 PC in the temperature range 20-400 °C at a heating rate of 20 K/min in the nitrogen atmosphere and the spectrum is shown in Figure 4.5. 7.000 mg sample was used for the present analysis. From this measurement, we found that the crystal was stable up to its melting point 186.1°C.
Figure 4.4 TG/DTA spectra of TTPC
Figure 4.5 DSC spectrum of TTPC
4.7.5 Optical assessment

The transmission spectrum of TTPC crystal was recorded in the range 200–1200 nm using SHIMADZU UV-1061 UV-Visible spectrophotometer. The recorded spectrum is shown in the Figure 4.6. It was observed from the spectrum that TTPC had a wide optical transmission window (200 – 1200 nm). It has good transparency 70 % and the lower cutoff wavelength of the crystal was found to be 235 nm, and thus to ascertain the fact that the crystal can be used for laser applications.

4.7.6 Nonlinear optical test using Kurtz powder technique

The second harmonic generation (SHG) conversion efficiency of TTPC was measured by Kurtz and Perry powder technique [13] using Nd:YAG laser as the source. The crystal was grounded into a homogenous powder of particles and densely packed between two transparent glass slides. A Q-switched Nd:YAG laser emitting a fundamental wavelength of 1064 nm (pulse width 8 ns) was allowed to strike on the sample cell normally. The SHG output 532 nm (green light) was finally detected by the photomultiplier tube.
Figure 4.6 Transmittance spectrum of TTPC
4.7.7 Mechanical behaviour

Microhardness measurements were carried out using Leitz Weitzler hardness tester fitted with a diamond indentor. The mechanical behaviour of TTPC crystal was analyzed by using Vickers microhardness test at room temperature. The crack free, smooth surface of TTPC crystal was chosen for this analysis. The crystal was mounted properly on the base of the microscope. Now the selected faces were indented gently by the loads varying from 10 to 60 g for a dwell period of 5 s. The plot of Vickers microhardness Vs. load is shown in Figure 4.7. The hardness was calculated using the relation

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

Where \( P \) is the applied load in kg and \( d \) is the diagonal length of the indentation impression in micrometer. However, with increasing load, the VHN value also simultaneously increased it was observed that the indentation marks were surrounded by a highly reflecting area [14, 15]. The measurement performed beyond a load of 60 g resulted in severe cracks. This might be due to the release of internal stress generated locally by indentation. A plot obtained between log (\( P \)) against log (\( d \)) gives a straight line, which is derived from the Meyer's law [15, 16], the relation connecting the applied load is given by \( P = ad^n \). Here \( n \) is the Meyer index or work hardening coefficient and \( a \) is the constant for a given material. The work hardening coefficient has been calculated from the slope of the straight line. The value of \( n \) is 2.02. From careful observations on various materials, Onitsch [17] pointed out that an \( n \) lies between 1 and 1.6 for hard materials and it is more than 1.6 for soft materials. This established that the TTPC crystals were soft substances.
Figure 4.7 Variation of Vicker's Microhardness number with applied load
4.7.8 Surface analysis

Chemical etching is a simple and very powerful tool to analyze the defects present in the growing crystal surfaces. Dislocations easily appear in crystals, especially in the initial stages of their growth [18]. Cut and polished specimen of TTPC was subjected to etching studies under identical conditions (110-face). Etching was carried out using deionized water as an etchant at room temperature. Once the damaged surface layer was removed during etching, a fresh surface appeared which in turn gave clear etch pits. The etched surfaces were dried by gently pressing them between two filter papers and then immediately examined and their microstructure was analyzed using an optical microscope in the reflection mode. The recorded images are given in Figures 4.8(a) and 4.8(b). From the fig. one can understand that the growth striations were observed. It might be due to variation of supersaturation during growth and it generated the growth striations in the crystal faces (Figure 4.8(a)). Etch pits were observed on the surface of the specimen. It may due to the insufficient molecules to build the basic blocks on the surface side of the specimen.
Etched (110) surfaces of TTPC

Figure 4.8(a) (etching time 10 s)  Figure 4.8(b) (etching time 20 s)
4.8 CONCLUSION

The tetra (thiourea) potassium chloride (TTPC) was successfully synthesized and good quality single crystals were grown in 20 days. From the single crystal X-ray diffraction analysis, it was found that the TTPC crystal has tetragonal system. The unit cell parameter values were also determined. The presence of various functional groups of TTPC was confirmed by the FTIR analysis. The thermal behaviour was assessed by TG/DTA analysis and found that the specimen might be useful for NLO application below its melting point 186 °C. Optical transmission range of TTPC was measured to be 200-1200 nm i.e. the grown crystal has a good optical transmission in the entire visible region. The Vicker's Microhardness was calculated in order to understand the mechanical stability of the grown crystals. Kurtz power nonlinear experiment confirmed that the TTPC crystal was a promising nonlinear optical material. The straight striations and kinks were observed on the crystal surface during etching.
REFERENCES


