CHAPTER 4

SYNTHESIS, GROWTH AND CHARACTERIZATION OF
BIS(TETRAETHYLAMMONIUM) BIS(HYDROGEN
L-TARTRATE) L-TARTARIC ACID MONOHYDRATE

4.1 INTRODUCTION

Materials that exhibit highly nonlinear optical (NLO) responses are currently of great scientific and technical interest (Halvorson et al. 1994, Marder et al. 1997, Slepkov et al. 2002, Bing Gu et al. 2003). In recent years, \( \pi \)-conjugated organic materials have attracted considerable interest because of their highly nonlinear optical properties and the fast response time of the nonlinearity (Gomes et al. 1996). The crystal structures of bis(tetraethylammonium) tartrate bis (thiourea) dihydrate, (Mei et al. 2002), Tetraethylammonium L-tartarate dihydrate (Rahman et al. 2008), (Tetraethylammonium L-malate 1.36-hydrate) were reported. L-Tartaric acid was a well known organic NLO material (Martin Britto Dhas et al. 2007). In the present work, bis (tetraethylammonium) bis (hydrogen L-tartrate) L-tartaric acid monohydrate was synthesised and grown by slow evaporation solution growth method for the first time and characterized.

In this chapter, the three dimensional structure of the grown crystal, determined by single crystal X-ray diffraction method is presented. In addition, the grown crystal was subjected to Fourier transform infrared, Optical, Thermal, Dielectric, Mechanical, Etching studies and Second harmonic generation test.
4.2 EXPERIMENTAL PROCEDURE

The title compound was synthesized using equimolar quantities of tetraethyl ammonium hydroxide and L-tartaric acid. The measured quantity of L-tartaric acid was dissolved in double distilled water until a saturated solution was obtained. Tetraethylammonium hydroxide (20% water) was then added to it drop wise. The mixture was stirred well at room temperature (RT) until a homogeneous solution was obtained. It was then stirred for 4h at 350 K in an oil bath and cooled to room temperature (RT). Figure 4.1 shows the structure diagram of Bis(tetraethylammonium) bis(hydrogen L-tartrate) L-tartaric acid monohydrate. It consists of two tetraethylammonium cations, balanced by two negative charges of the L-tartrate anions. Also present in the asymmetric unit are a molecule of L-tartaric acid and a water molecule.

![Structure diagram of Bis(tetraethylammonium) bis(hydrogen L-tartrate) L-tartaric acid monohydrate](image)

Figure 4.1 Structure diagram of Bis(tetraethylammonium) bis(hydrogen L-tartrate) L-tartaric acid monohydrate

The cooled solution was then filtered and the filtrate was covered using a thick parafilm sheet, in order to control the evaporation rate at RT in a constant temperature bath. Good quality single crystals of title compound were obtained after a month (11 × 2 × 2 mm³). The harvested single crystals of bis(tetraethylammonium) bis(hydrogen L-tartrate) L-tartaric acid monohydrate are shown in Figure 4.2.
CHARACTERIZATION

4.3.1 Single Crystal XRD

Suitable crystals of TELT were selected for single crystal XRD studies. The intensity data were collected at 173K (-100°C) on a Stoe Mark II-Image Plate Diffraction System (Stoe and Cie 2009) equipped with a two-circle goniometer and using MoKα graphite monochromated radiation ($\lambda = 0.71073$ Å). The experiment was performed with Image plate distance 130 mm, $\omega$ rotation scans $0 - 180^\circ$ at $\phi$ $0^\circ$, and $0-112.0^\circ$ at $\phi$ $90^\circ$, step $\Delta\omega = 1.0^\circ$, exposures of 3 mins per image, $2\theta$ range 1.76-52.59°, $d_{\text{min}} - d_{\text{max}} = 23.107 - 0.802$ Å.

The structure was solved by Direct methods using the programme SHELXS-97. The refinement and all further calculations were carried out using SHELXL-97 (Sheldrick 2008). Further crystal data, experimental conditions and structural refinement parameters are presented in Table 4.1.
Table 4.1  Crystal data and structure refinement for TELT

|                      | 2(C₈H₂₀N), C₄H₆O₆, 2(C₄H₅O₆), H₂O |
|----------------------|--------------------------------------|
| Formula Weight       | 726.76                               |
| Crystal System       | Monoclinic                           |
| Space group          | P₂₁                                  |
| a, b, c [Å]          | 7.5725(4)Å, 27.7907(13)Å, 8.7620(6)Å |
| alpha, beta, gamma [°]| 90°, 99.884(5)°, 90°                |
| V [Å³]               | 1816.55(18)Å³                        |
| Z                    | 2                                    |
| D(calc) [g/cm³]      | 1.329 g/cm³                          |
| Mu(MoKα) [/mm]       | 0.112 mm⁻¹                           |
| F(000)               | 784                                  |
| Crystal Size [mm]    | 0.25 × 0.32 × 0.45 mm³               |

**Data Collection**
- Temperature (K): 173 K
- Radiation [Å]: MoKα 0.71073 Å
- Theta Min-Max [°]: 1.5-25.7°
- Dataset: -9:9; -33:33; -10:10
- Tot., Uniq. Data, R(int): 20250, 3502, 0.072
- Observed data [I > 2.0 sigma(I)]: 3116

**Refinement**
- Nref, Npar: 3502, 469
- R, wR2, S: 0.0321, 0.0639, 1.03
- w = 1/[σ²(F)+σ²(P)] where P = (σ²(A) + 2σ²(C))/3
- Max. and Av. Shift/Error: 0.00, 0.00
- Min. and Max. Resd. Dens. [e/Å³]: -0.20, 0.17 Å³

The water H-atoms were located in a difference electron density map and were refined freely. The OH and C-bound H-atoms were included in calculated positions and treated as riding atoms: O-H = 0.84 Å, C-H = 1.0,
0.99 and 0.98 Å for CH, CH₂ and CH₃, respectively, with \( U_{\text{iso}}(H) = k \times U_{\text{eq}}(O,C) \), where \( k \) is 1.5 for OH and CH₃ H-atoms, and 1.2 for all other H-atoms. The non-H atoms were refined anisotropically, using weighted full-matrix least-squares on \( F^2 \). An empirical absorption correction was applied using the MULscanABS routine in PLATON (Spek 2003). The molecular structure of the title compound is illustrated in Figure 4.3. The asymmetric unit is composed of two tetraethylammonium cations, two hydrogen L-tartrate anions, a molecule of L-tartaric acid and a water molecule. The various moieties are linked by O—H···O hydrogen bonds.

![Illustration of molecular structure and crystallographic numbering scheme](image)

**Figure 4.3** Illustration of molecular structure and crystallographic numbering scheme, with displacement ellipsoids are drawn at the 50% probability level

In the crystal two-dimensional networks (Figure 4.4) are formed via O—H···O hydrogen bonds and C—H···O interactions involving the water
molecule, the hydrogen L-tartrate anions and the L-tartaric acid molecules. These layers stack along [001] are separated by tетraethylammonium cations, which are also involved in C—H···O interactions with the anions and the L-tartaric acid and water molecules. This arrangement is similar to that in the crystal structure of tетraethylammonium hydrogen L-tartrate dihydrate, which has been reported previously (Rahman et al 2008).

![Illustration of the crystal packing viewed along the a-axis. The O-H…O hydrogen bonds are shown as dashed lines](image)

**Figure 4.4** Illustration of the crystal packing viewed along the a-axis. The O-H…O hydrogen bonds are shown as dashed lines

### 4.3.2 FT-IR Spectrum

The FT-IR spectral analysis of TELT was carried out to investigate the presence of functional groups and their vibrational modes. The spectrum was recorded in the region 4000 - 400 cm\(^{-1}\) (Perkin Elmer Spectrum RX1 spectrophotometer equipped with He-Ne source, KBr beam splitter and LiTaO\(_3\) detector). The sample was prepared by mixing it with KBr into a pellet form. The recorded spectrum is shown in Figure 4.5. The broad absorption band, between 3500 and 3000 cm\(^{-1}\), is due to the O-H and N-H stretching vibrations and the intermolecular H-bonding among the water molecules in the crystals. The strong but broad peak at 3324 cm\(^{-1}\) is due to the presence of O-H stretching in the carboxyl group (Silverstein and Webster, 1998). The small shoulder at 3273 cm\(^{-1}\) is due to primary amine of N-H
stretching. Sharp peak occurring at 2987 cm\(^{-1}\) is due to alkyl C-H stretching. The sharp peak at 1732 cm\(^{-1}\) is due to free tartaric acid C = O stretch. The N-H bending vibrations of tartaric acid are attributed to 1578 cm\(^{-1}\) (Haja Hameed and Lan 2004). The peak assigned at 1405 cm\(^{-1}\) is due to C-H bending vibration. The absorption peaks at 1266 cm\(^{-1}\) and 1003 cm\(^{-1}\) are due to –COO- and C-O modes of tartaric acid. The sharp peaks at 1135 and 1067 cm\(^{-1}\) are also due to C-O stretching. The peak at 523 cm\(^{-1}\) is due to torsional N-H oscillation. The peak below 1000 cm\(^{-1}\) are due to different bending vibration of the title compound.

![FTIR spectrum of Bis(tetraethylammonium) bis(hydrogen L-tartrate) L-tartaric acid monohydrate](image)

**Figure 4.5** FTIR spectrum of Bis(tetraethylammonium) bis(hydrogen L-tartrate) L-tartaric acid monohydrate

### 4.3.3 Optical Properties

#### 4.3.3.1 Absorbance

The UV–Vis transmittance spectrum was recorded for the grown TELT crystal using a SHIMADZU UV-2501 PC, UV–Vis spectrophotometer
in the range 290-2225 nm. The plot of absorbance (a.u) with wavelength (nm) shown in Figure 4.6(a), is obtained with a crystal of 2 mm thick. NLO material can be of utility only if it has a wide transparency window without any absorption in the fundamental and second harmonic wavelengths and preferably with the lower limit of transparency window being well below 400 nm. From the absorbance spectrum, it is observed that crystal absorbs largely within UV region but moderately in the VIS-NIR region. The cut-off wavelength of TELT is 252 nm. In general the UV–Vis range from 200 to 400 nm is very important for the realization of second harmonic generation (SHG). From the graph, it is evident that the crystal has a transparency window from 252 nm suggesting the suitability of the title crystal for optical application.

![Absorbance spectrum of Bis(tetraethylammonium) bis(hydrogen L-tartrate) L-tartaric acid monohydrate single crystal](image)

**Figure 4.6(a)** Absorbance spectrum of Bis(tetraethylammonium) bis(hydrogen L-tartrate) L-tartaric acid monohydrate single crystal
4.3.3.2 Optical band gap

Optical band gap of the material was calculated from the transmittance spectrum. The measured transmittance (T) was used to calculate the absorption coefficient (α) using the equations 2.1 and 2.2 (given in the chapter 2). The band gap was calculated from the plot between hv and $(αhν)^{1/2}$ as shown in the Figure 4.6(b). The optical band gap is equal to 3.6 eV.

Figure 4.6(b) The optical band gap of Bis(tetraethylammonium) bis(hydrogen L-tartrate) L-tartaric acid monohydrate single crystal (plot between $(αhν)^{1/2}$ and hv for showing the optical band gap)
4.3.3.3 Refractive Index (n)

The refractive index can be measured from the reflectance of the material. The reflectance (R) in terms of the absorption coefficient can be obtained from the equations (2.3 and 2.4) used in the chapter 2. The dependence of refractive index (n) with photon energy for TELT crystal is shown in Figure 4.6 (c). The refractive index increases with increasing wavelength. The refractive index (n) is 1.24 at 4.14 eV.

![Figure 4.6 (c) The dependence of refractive index (n) with photon energy. Inset (d) Refractive index (n) with wavelength for TELT](image)

4.3.4 Thermal Analysis

The thermal behaviour of the title crystal was studied by TGA and DTA using ZETZSCH—Geratebau GmbH Thermal Analyzer. The sample was heated at nitrogen atmosphere in alumina crucible at a heating rate of 20 K min⁻¹. The TG curve depicted in Figure 4.7 shows two stages weight
loss when heated between room temperature and 900°C. The first weight loss of 5.136% is due to removal of water molecules. Hence the material is thermally stable up to 192°C and above this temperature the material loses its weight sharply. As can be seen from the DTA curve in the Figure 4.7, the material undergoes an endothermic transition at 128.86°C due to loss of lattice water. The sharp weight loss observed at 224.20°C is attributed to decomposition of the compound. The sharp endothermic peaks in the DTA trace nearly coincide with decompositions shown in the TGA trace.

![Image of TG trace of Bis(tetraethylammonium) bis(hydrogen L-tartrate) L-tartaric acid monohydrate](image)

**Figure 4.7** TG trace of Bis(tetraethylammonium) bis(hydrogen L-tartrate) L-tartaric acid monohydrate

### 4.3.5 Hardness

The microhardness characterisation is extremely important as far as the fabrication of devices is concerned. Hardness of a material is the measure of resistance when it offers to local deformation. Indentations were made on
(1 0 1) plane of TELT crystal using Reichert MD 4000E ultra microhardness tester fitted with a Vicker’s diamond pyramidal indenter. The indentations were made at room temperature with a constant indentation time of 2 second. The dimensions of both diagonals of an indentation were measured, and the average dimension d was calculated from all diagonals made at a particular load P. The Vickers hardness is calculated using the relation given in equation 1.11 (given in the chapter 1). Figure 4.8(a) shows that apparent microhardness increases with increasing applied test loads. This type is called a reverse indentation size effect (called reverse ISE hereafter). The indented surface of TELT sample gives cracks around indentations. The crack length formed on the surface of the crystal is shown in Figure 4.8(b). At 50 g the sample gets totally deformed which is clearly seen from Figure 4.8(c).

![Graph](image)

**Figure 4.8(a)** Variation of microhardness (H_V) with the applied load (P) for TELT
The Meyer's index number was calculated from the equations (1.12 and 1.13), which relate the load and indentation diagonal length. In order to calculate the value of \( n \), the graph is plotted between log \( P \) and log \( d \) (Figure 4.8(d)) and the slope gives the value of \( n \) as 1.9. \( H_v \) should increase with the increase of \( P \) if \( n > 2 \) and decrease if \( n < 2 \). The \( n \) value agrees well with the experiment. According to Onitsch (1947) ‘\( n \)’ should lie between 1 and 1.6 for harder materials and above 1.6 for softer materials. Thus TELT belongs to the soft material category.
For a crystal with well-defined cracks, the resistance to fracture indicates the toughness of a material. According to Ponton and Rawling (1989) fracture toughness \( K_c \) is dependent on the ratio of \( c/a \), where \( c \) is the crack length and \( a \) is the half-diagonal length of the square indentation. For the median crack system, the fracture toughness \( c/a \) is calculated using the equation 1.14 (given in chapter 1) (when \( c/a \geq 2.5 \)), whereas for Palmqvist configuration, \( K_c \) is obtained by the relation given in equation 1.15 (given in chapter 1) (when \( c/a \leq 2.5 \)). The brittleness index \( B_i \) is calculated using the relation (given in chapter 1) 1.16.

From the hardness values, the yield strength \( \sigma_y \) can be calculated, depends on Meyer's index \( n \). For \( n > 2 \), the yield strength \( \sigma_y \) may be calculated using the expression (given in chapter 1) 1.17. The elastic stiffness constant \( (C_{11}) \) for different loads calculated using Wooster's empirical formula \( C_{11} = H_v^{7/4} \) (Wooster 1953) is presented in Table 4.2. The stiffness constant increases with hardness which gives an idea about the bonding between neighbouring atoms.

### Table 4.2 Mechanical properties of A TELT crystal under various Loads

| Load (g) | \( H_v \) (MPa) | \( a \) (\( \mu \)m) | crack length \( c \)(\( \mu \)m) | \( K_c \) (MPa.m\(^{1/2}\)) | \( \sigma_y \) (kg/mm\(^2\)) | \( B_i \) (\( \mu \)m\(^{-1/2}\)) | \( C_{11} \) |
|---------|-----------------|--------------------|-------------------------------|-------------------|-----------------|-------------------|---------|
| 1       | 49              | 9.37               | -                             | -                 | 1.666           | -                 | 16.71   |
| 3       | 135.24          | 9.92               | -                             | -                 | 4.6             | -                 | 98.80   |
| 5       | 253.82          | 9.455              | 10.07                         | 2.407             | 8.633           | 105.4             | 297.35  |
| 10      | 282.24          | 12.67              | 27.17                         | 0.152             | 9.6             | 1851.8            | 358.04  |
4.3.6 Etching Studies

Etching study was performed on TELT by dipping the crystal in water for a few seconds at room temperature. Etch patterns were photographed under an optical microscope in the reflected light and the observed well defined parallel etch pits found on the (1 0 1) plane as shown in Figure 4.9. When etched with water for 10 s, shape of the observed etch pits is close to parallel and layer growth. The shape of the etch pattern indicates the direction of the dislocation lines. Further increasing the etching time to 30s and 60s, the pattern remains the same but the numbers of etch pits decrease. While increasing the etching time observed etch patterns are of well defined shape. The observed etch pits, due to layer growth, confirmed the two-dimensional nucleation (2D) mechanism with less dislocations. Similar etch patterns were reported for L-arginine trifluoroacetate single crystal (Murkerji and Kar 1999).

![Etch patterns observed on (1 0 1) plane of TELT Single Crystal with water as an etchant before etching, 30s and 60s](image)

4.3.7 Second Harmonic Generation Test

The SHG behaviour was confirmed with powdered samples of TELT by the Kurtz - Perry powder technique (Kurtz and Perry 1968) from the
output of the Nd: YAG (λ = 1064 nm) with pulse duration of 10 ns laser beam having the bright green emission (λ = 532 nm). The second harmonic signal of 3.92 mV for TELT was obtained for an input energy of 4.9 mJ/pulse. But the standard KDP crystal gave a SHG signal of only 25 mV/pulse for the same input energy. The SHG of this material is low compared to standard material even though it crystallizes in noncentrosymmetric with space group P2₁.

4.4 CONCLUSION

Bis(tetraethylammonium) bis(hydrogen L-tartrate) L-tarataric acid monohydrate (TELT) was synthesised and grown successfully by slow evaporation solution growth method for the first time in the literature. Single crystal X-ray diffraction confirmed the grown crystal belongs to Monoclinic system with space group P2₁, \( a = 7.5725 \) (4) Å, \( b = 27.7907 \) (13) Å, \( c = 8.7620 \) (6) Å, \( \beta = 99.884 \) (5)°, \( V = 1816.55 \) (18) Å³. Fourier transform infrared spectroscopy (FT-IR) revealed the functional group of the grown crystal. The lower optical cut off wavelength is found to be 252 nm and optical band gap is 3.6 eV. Thermogravimetric (TG) and differential thermal analysis (DTA) studies revealed that TELT is thermally stable up to 192°C. From the mechanical test and the work hardening coefficient (n), fracture toughness (\( K_c \)), Brittleness index (\( B_i \)), Yield strength (\( \sigma_y \)) and elastic stiffness constant (\( C_{11} \)) were evaluated. Etching studies revealed layer growth, which confirmed the two-dimensional nucleation (2D) mechanism with less dislocation. The second harmonic generation was confirmed by Kurtz-Perry technique. The SHG of this material is low compared to standard material even though it crystallizes in noncentrosymmetric with space group P2₁.