CHAPTER - 3
3. GROWTH AND CHARACTERIZATION OF TARTARIC ACID BASED SINGLE CRYSTALS

3.1 Introduction

Naturally occurring L-Tartaric acid or levotartaric acid is an alpha-hydroxy-carboxylic acid. It is a chiral organic acid, which has molecules that are not superimposable on their mirror images and capable of easily dissociating in water. The structure of L-tartaric acid was resolved by Okaya et al (Okaya et al 1966) and the crystal belongs to the monoclinic system (Martin Britto Dhas et al 2007). L-tartaric acid crystals have noncentrosymmetric space group and the 3D molecular structure of L-tartaric acid is depicted in Figure 3.1.

![Figure 3.1 3D molecular structure of L-tartaric acid](image)

A number of amino acids and metal coordinates mixed with tartaric acid crystals, as follows, L-asparagine tartrate, L-alanine tartrate, L-lysine tartrate, calcium tartrate and strontium tartrate etc. have interesting physico-chemical properties were synthesised and reported earlier (Natarajan et al 2010, Rajesh et al 2013, Debrus et al 2005, Suryanarayana and Dharmaprakash 2000, Arora et al 2005). In the present work, L-Histidinium L-Tartrate Hemihydrate (LHT) and Sodium Hydrogen L-Tartrate Monohydrate (SHT) crystal were synthesised by slow evaporation technique. The spectral, optical, electrical, mechanical and thermal studies with kinetic parameters were discussed in detail.
3.2 Growth and Physic-chemical Properties of L-Histidinium L-Tartrate Hemihydrate Single Crystal

3.2.1 Experimental

3.2.1.1 Synthesis and Crystal Growth

AR grade materials were used for the synthesis and growth of L-histidinium L-Tartrate hemihydrate (LHT) crystal by slow evaporation technique. L-histidine and L-tartaric acid were taken in equimolar ratio and dissolved in deionized water under constant stirring for 4h. The resultant solution was filtered and allowed to evaporate at room temperature. Optically good quality single crystals of dimension 1.2×1×0.4cm³ were harvested in a time span of 25 days. The chemical reaction involved in the formation of crystal is given in Equation 3.1. The purity of the synthesized salt was increased by the repeated recrystallisation process. The photograph of the as grown LHT crystal is shown in Figure 3.2.

\[
\text{C}_6\text{H}_9\text{N}_3\text{O}_2 + \text{C}_4\text{H}_6\text{O}_6 \rightarrow (\text{C}_8\text{H}_{10}\text{N}_3\text{O}_2)^+ \cdot (\text{C}_4\text{H}_5\text{O}_6)^- \cdot 0.5\text{H}_2\text{O} \quad (3.1)
\]

<table>
<thead>
<tr>
<th>Crystal data</th>
<th>LHT</th>
</tr>
</thead>
<tbody>
<tr>
<td>Space group</td>
<td>C2</td>
</tr>
<tr>
<td>a(Å)</td>
<td>22.92</td>
</tr>
<tr>
<td>b(Å)</td>
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<tr>
<td>c(Å)</td>
<td>7.62</td>
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<tr>
<td>β(degree)</td>
<td>96.84</td>
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<tr>
<td>Crystal system</td>
<td>monoclinic</td>
</tr>
<tr>
<td>Volume (Å³)</td>
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</table>

3.3 Results and Discussion

3.3.1 Single Crystal X-ray Diffraction Analysis

The unit cell parameter and space group of the crystal were determined by single crystal X-ray diffraction, using BRUKER axs SMART APEXII diffractometer. The single
crystal XRD data of LHT indicates that, the crystal is of monoclinic in structure with the space group of C2. The crystallographic data are given in Table 3.1 and it agrees well with the reported values (Marchewka et al 2003).

3.3.2 Powder X-ray Diffraction Analysis

The crystalline nature and reflection planes of the grown LHT crystal were identified by the Powder X-Ray Diffraction pattern (PXRD) of the powdered sample by using PHILIPS ‘X’ Pert Pro Radiation CuKα X-ray diffractometer in the range of 10-70° with a scan speed of 1°/min and the peaks were indexed by using “powder X” software. Figure 3.3 shows the indexed X-ray powder diffraction pattern of LHT single crystal. The sharp and intense peaks in the pattern confirm the high crystallinity and good quality of the grown crystal (Parasuraman et al 2011).

![Figure 3.3 Powder X-ray diffraction pattern of LHT](image)

3.3.3 FTIR Studies

Figure 3.4 shows the Fourier transform infrared spectrum of LHT crystal which was recorded in the range between 4000 and 400 cm\(^{-1}\) using SHIMADZU-8400S Spectrophotometer. The FTIR spectra consist of two major regions (i) Group frequency region (ii) Fingerprint region. Group frequencies are vibrations that are associated with
certain structural units such as -CH₃,-NH₂, -C=Н etc. and appear fairly constant regions in the spectra. The molecules having similar groups show their vibration in the form of bands is called a finger print region. The peak at 3492cm⁻¹ represents the asymmetric stretching vibration of water molecule (Anandan et al 2012). The C-H aliphatic stretching vibration is observed at 2931cm⁻¹ (Madhavan et al 2007). The peaks present at 1648 and 2867cm⁻¹ in the spectra are assigned to NH₃⁺ asymmetric bending and CH₂ asymmetric stretching vibration respectively (Madhavan et al 2007, Rajendran et al 2001). The peaks observed at 1468 and 830cm⁻¹ in the spectra are attributed to O-H and ring deformation (Martin Britto Dhas et al 2007, Anandan et al 2012). The Peaks observed at 1232 and 1077cm⁻¹ are due to COO⁻ and C-O stretching of tartrate anion (Xu et al 2003, Anandan et al 2012). These results confirm that the L-histidine exists in Zwitter ionic form in the grown crystal and the vibrational assignment agrees well with the reported values (Marchewka et al 2003).

Figure 3.4 FTIR spectrum of LHT

3.3.4 UV-vis-NIR Studies

The absorption of UV and visible light by the molecule involves the promotion of the
e in the  and  orbital from the ground state to higher state gives the information about the structure of the molecule (Sankar et al 2007). The absorption spectra of LHT crystal was recorded using Lambda UV-vis-NIR spectrometer in the frequency region 190-1100nm, with a scan speed of 960nm/min and a data interval of 1nm as shown in Figure 3.5.

It is evident from the spectrum that the crystal has low absorption in the entire visible and IR region, which is the mandatory requirement for the material having NLO properties (Vijayan et al 2003). The lower cutoff wavelength of the as grown crystal is found at 230nm and the corresponding band gap value was calculated as 5.39eV using the Equation 3.2.
\[ E_g = \frac{\hbar c}{\lambda_{\text{max}}} \text{ eV} \]  

where \( \lambda_{\text{max}} \)-lower cutoff wavelength, \( \hbar \)-Planck’s constant, \( c \)-velocity of light. The band gap energy was also estimated by Tauc plot of graph between \( h\nu \) versus \( (a h\nu)^2 \) as shown in Figure 3.6. Intercept of the linear portion of the plot on the \( h\nu \) axis gives the value of direct optical band gap energy \( E_g \) of the grown crystal as 5.39eV. The larger optical band gap value shows that the defect concentration in the grown crystal is very low (Parthasarathy et al 2012).

3.3.5 Fluorescence Studies

The fluorescence emission spectrum of LHT crystal was recorded using LS45 Spectrofluorometer in the range of 250-500nm at the excitation wavelength of 230nm as shown in Figure 3.7. The spectrum shows three emission peaks at the wavelengths of about 402, 470 and 511nm. A high intense peak was observed in the visible region at 470nm which indicates the blue emission. A moderate and a small peak were observed on either side of the high intense peak, which corresponds to violet and green emission. These visible emissions of the grown crystal might be used for optoelectronic devices (Rajendran and Gajendiran 2015).

![Fluorescence spectrum of LHT](image)
3.3.6 SHG Studies

The second harmonic conversion efficiency of the grown crystals is confirmed by the Kurtz and Perry powder method (Kurtz and Perry 1968). A Q-switched Nd:YAG laser beam of wavelength 1064nm, with an input power of 450mJ, a pulse width of 10ns and a repetition rate of 10Hz is made to fall normally on the powdered sample of the grown crystals. The second harmonic generation was confirmed by the emission of green light of wavelength 532nm. The powdered material of potassium dihydrogen phosphate (KDP) was used as a reference material in order to compare the efficiency of the as grown crystal. The comparative SHG efficiency of the as grown LHT crystal is found to be 0.5 times than that of the KDP crystal.

3.3.7 Thermal Studies

Thermo Gravimetric Analysis (TGA) and Differential Thermal Analysis (DTA) of LHT were carried out in nitrogen atmosphere from 25-978°C using SDT Q600 V8.0 Build 95. The powdered sample of 4.6mg of LHT was used for this analysis. The TGA and DTA traces of LHT are shown in Figure 3.8.

![Figure 3.8 TG/DTA analysis of LHT](image-url)
The TGA curve illustrates a gradual weight loss below 174°C which is attributed to the loss of lattice water. The first stage of weight loss occurs between 174-260°C corresponds to the loss of 37.63%, which is due to the decomposition and volatilization of the CO and NO₂ gases. The second stage between 260-470°C is connected with mass loss of 60%, which indicates the vaporization and burning of volatile gases such as CO₂ and NH₃ produced from the thermal degradation of the compound (Urit Charoen-In et al 2015). The last stage of the decomposition extended up to 978°C and then the entire compound was decomposed.

From DTA graph, an endothermic peak is observed at 178.55°C which is due to the melting point of the material. The results of the DTA analysis are being consistent with the TGA data. The sharpness of the endothermic peaks shows the good degree of crystalline of the sample (Manikandan and Dhanuskodi 2007). It undergoes three more irreversible endothermic transitions at 208, 225 and 291°C which indicate the major decomposition of the material at various stages respectively. LHT crystal is fully stable up to 178°C and hence, the crystal can be exploited for applications below 178°C.

The kinetic parameters, namely activation energy (E), enthalpy (ΔH), entropy (ΔS) and Gibb’s free energy of activation (ΔG) were obtained from the first stage of decomposition by using TG based model, Coats-Redfern relation (Coats and Redfern 1964). The present study claims its significance for being the first attempt in the thermo analytical studies of organic L-histidinium L-tartrate hemihydrate crystal.

For n=1

\[ \log \left[ \frac{-\log(1-\alpha)}{T^2} \right] = \log \left( \frac{AR}{\theta E} \right) \left( \frac{1-2RT}{E} \right) - \frac{E}{2.303RT} \]  

(3.3)

where \( \alpha \) is the fraction of material reacted = \( \frac{W-W_0}{W-W_f} \), \( W_0 \) is the initial weight, \( W \) is the weight at time ‘t’, \( W_f \) is the final weight, \( n \) is the order of the reaction, \( R \) is the gas constant, \( E \) is the activation energy of the reaction and \( \theta \) is the linear heating rate. A graph between \( \log [-\log (1-\alpha)/T^2] \) against 1/T (Figure 3.9) results in a straight line and the slope
value (n) is found by least square fitting method (Krishnan et al 2013). The $\log \left(\frac{AR}{\theta E}\right)$ value is constant for most values of E and for the temperature ranging over in which the reaction occurs.

![Figure 3.9 Plot of 1/T vs Log [-Log (1-\(\alpha\)/T\(^2\))] of LHT](image)

The values of $E_a$, the activation energy of the reaction can be calculated using the slope value of the graph is,

$$E_a = 2.303 \times R \times \text{slope}$$

(3.4)

By knowing the value of the intercept, Arrhenius constant, Entropy, Enthalpy, Gibb’s free energy can be calculated by using,

$$\frac{AR}{\alpha E} \left(1 - \frac{2RT}{E}\right) = e^{\text{intercept}}$$

(3.5)

By following the above Equation 3.5, other standard values of Entropy, Enthalpy, and Gibb’s free energy can be calculated using the formulas given below.

Entropy,

$$\Delta S = 2.303 \times R \times \log_{10} \left(\frac{A_h}{kT_m}\right)$$

(3.6)

where k is the Boltzmann constant ($1.3806 \times 10^{-23}$ m\(^2\) kg s\(^{-2}\) K\(^{-1}\)), h is the Planck constant, T is the middle temperature and A is the Arrhenius constant.

Enthalpy,

$$\Delta H = E - 2RT$$

(3.7)

Gibb’s free energy,

$$\Delta G = \Delta H - T\Delta S$$

(3.8)
The calculated values of $E_a$, $A$, $\Delta S$, $\Delta H$ and $\Delta G$ for the first stage of decomposition of the crystal are given in Table 3.2. The activation energy ($E_a$) is negative, which reveals that the energy required to make the reaction is very less. The value of enthalpy ($\Delta H$) indicates the absorption of energy in the reaction. The Gibb’s free energy, $\Delta G<0$ proves that the reaction is spontaneous. The calculated values of kinetic parameters of LHT would be useful in thermal decomposition optimization.

### Table 3.2 Kinetic parameters of LHT

<table>
<thead>
<tr>
<th>Kinetic parameters</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Activation energy ($E$) in kJ mol$^{-1}$</td>
<td>-115.96</td>
</tr>
<tr>
<td>Frequency factor ($A$) in kS$^{-1}$</td>
<td>-107.31</td>
</tr>
<tr>
<td>Enthalpy of activation ($\Delta H$) in kJ mol$^{-1}$</td>
<td>209.85</td>
</tr>
<tr>
<td>Entropy of activation ($\Delta S$) in J K$^{-1}$ mol$^{-1}$</td>
<td>-123.76</td>
</tr>
<tr>
<td>Gibb’s free energy ($\Delta G$) in kJ mol$^{-1}$</td>
<td>-222.13</td>
</tr>
</tbody>
</table>

#### 3.3.8 Dielectric Studies

The dielectric properties of the sample were characterized by the HIOKI 3532-50 LCR HITESTER. Sample with the thickness 0.24cm$^3$ and the area of cross section 4.40cm$^3$ was coated with silver on the opposite faces are placed between the two copper electrodes, to form parallel plate capacitors. The capacitances of the samples were measured by varying the frequencies from 50Hz to 5MHz for different temperatures (308, 313, 318 and 323K). The dielectric constant of the crystal is calculated using the Equation as:

$$\varepsilon_r = \frac{C_p t}{\varepsilon_0 A}$$  \hspace{1cm} (3.9)

By knowing the value of parallel plate capacitance ($C_p$) of the sample, thickness ($t$) of the sample, permittivity of free space ($\varepsilon_0$) and area of cross section ($A$) of the sample, $\varepsilon_r$ can be calculated.

The response of dielectric constant as a function of Log frequency at different temperatures is shown in Figure 3.10. As the frequency increases, dielectric constants
decrease exponentially and attain lower values at high frequency. At lower frequencies the four types of polarizations namely electronic ($\alpha_e$), ionic ($\alpha_i$), orientational ($\alpha_o$) and space charge polarization ($\alpha_s$) will be active and there is a gradual decrease of these polarizations at higher frequencies (Senthil Pandian and Ramasamy 2010). The change in the value of dielectric constant at lower frequency is due to space charge polarization which is active at lower frequency (Rajesh et al 2009). It is clear that the variation of dielectric constant with varying temperature is very less which suggests that the sample possesses high chemical homogeneity (Hiremath and Venkataraman 2003).

In Figure 3.10 some peaks are observed, may be correlated with the resonance effects on electro-optic coefficients, at certain frequencies. The reason for this may be that for certain critical frequencies of the applied field, standing waves are established in the crystal through the inverse piezoelectric effect and these critical frequencies are dependent on the dimensions of the sample studied (Martin Britto Dhas et al 2008). The resonance of these stationary waves with the applied electric field at selected frequencies leads to the observed peaks (Brahadeeswaran et al 2000). Similarly, the dielectric loss was studied as a function of Log
frequency at different temperature and is shown in Figure 3.11. It is calculated by the relation,

$$\tan \delta = \varepsilon_0 D$$  \hspace{1cm} (3.10)

where $\tan \delta$ is the tangent loss, $\varepsilon_0$ is the permittivity of free space and $D$ is the dissipation factor. It suggests that dielectric loss is strongly depending on the frequency of the applied field similar to that of dielectric constant. The low value of dielectric loss at high frequency for these samples suggests that the samples possess lesser defects (Martin Britto Dhas et al 2007).

### 3.3.9 Mechanical Studies

The mechanical behaviour of the grown crystal was measured with a diamond indenter using Shimadzu HMV-2 Vicker’s indentation tester. The well polished crystal was mounted on the platform of the micro hardness tester and loads of different magnitudes from 25-100g were applied over a fixed interval time of 10s. The Vickers hardness number of the grown crystals was calculated using the relation,

$$H_v = 1.854 \frac{P}{d^2} \text{ (Kg/mm}^2\text{)}$$  \hspace{1cm} (3.11)

where $H_v$ is the Vickers microhardness number, $P$ is the applied load and $d$ is the average diagonal length of the indentation impression, 1.854 is a constant of a geometrical fraction for the diamond pyramidal indenter. A graph was plotted between hardness number ($H_v$) and applied load $P$ as shown in Figure 3.12. From the graph, it is found that the hardness value increases with the increase of load exhibits the Reverse Indentation Size Effect (RISE) (Gong and Li 2000). The relation between load and size of indentation is given by Meyer’s law (Meyer 1908) as:

$$P = K_1 d^n$$  \hspace{1cm} (3.12)

$$\log P = \log K_1 + n \log d$$  \hspace{1cm} (3.13)
where $K_1$ is the material constant and $n$ is Meyer's index. The value of $n$ is calculated using Equation 3.13 from the slope of the graph plotted between Log P and Log d (Figure 3.13) and is found to be 3.5. According to Onitsch (Onitsch 1947), ‘$n$’ should lie between 1 and 1.6 for harder materials and above 1.6 for softer materials. The value of ‘$n$’ indicates that the LHT crystal belongs to the soft material category (Onitsch 1947, Hanneman 1941).

Hays and Kendall's theory (Hays and Kendall 1973) of resistance pressure, explains a relationship between indentation test load ($P$) and indentation size ($d$) by assuming the following Equation:

$$P - W = K_2 d^2 \tag{3.14}$$

Substituting the expression of Equation 3.12 for $P$ in Equation 3.14, we have

$$W = K_1 d^n - K_2 d^2$$

$$d^n = (K_2/K_1) d^2 + (W/K_1) \tag{3.15}$$

where $W$ is the sample resistance pressure and represents the minimum load that causes an indentation, $K_2$ is another constant. The plot of $d^n$ against $d^2$ is a straight line having a slope $K_2/K_1$ and intercept $W/K_1$ (Figure 3.14). The hardness parameters were calculated and are
tabulated in 3.3. The yield strength \( (\sigma_v) \) of the material was calculated using the formula (Cahoon et al 1971),

\[
\sigma_v = \frac{H_v}{2.9} \left[ 1 - (n - 2) \right] \left[ \frac{12.5(n-2)}{1-(n-2)} \right]^2
\]

(3.16)

which is a measure of minimum stress required to resist permanent deformation. The elastic stiffness constant \( (C_{11}) \) were calculated using the hardness number with Wooster’s empirical relation (Wooster 1953),

\[
C_{11} = (H_v)^{7/4}
\]

(3.17)

which gives an idea about the tightness of bonding between the neighbouring atoms. The calculated mechanical properties (Revathi and Rajendran et al 2013) are presented in Table 3.4 indicates the strong binding forces between the ions of LHT.

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**Table 3.3 Hardness parameters of LHT**

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Values</th>
</tr>
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<tbody>
<tr>
<td>( ^{\circ}n )</td>
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<tr>
<td>( K_1 ) (Kg/m)</td>
<td>2.1645×10(^2)</td>
</tr>
<tr>
<td>( K_2 ) (Kg/m)</td>
<td>8.1085×10(^4)</td>
</tr>
<tr>
<td>( W ) (Kg)</td>
<td>4.0711×10(^4)</td>
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**Table 3.4 Mechanical properties of LHT**

<table>
<thead>
<tr>
<th>Load P(g)</th>
<th>( C_{11} ) (GPa)</th>
<th>( \sigma_v ) (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>1.2393</td>
<td>4.6323</td>
</tr>
<tr>
<td>50</td>
<td>2.2416</td>
<td>6.4994</td>
</tr>
<tr>
<td>100</td>
<td>3.4729</td>
<td>8.3468</td>
</tr>
</tbody>
</table>

---

Figure 3.14 Plot of \( d^n \) vs \( d^2 \) of LHT
3.3.10 Etching Studies

Etching is the selective dissolution of the crystal which reveals the crystal symmetry and lattice defect patterns observed on the surface, like step pattern, spirals, hillocks and grain boundaries, etc. yield considerable information on the growth process and growth mechanism of the crystal (Sivashankar et al 2009, Dhanaraj and Rajesh 2011). When a surface is etched, well defined etch patterns are produced at the dislocation sites.

The etch pit patterns of the LHT crystal were found by using water as an etchant for 5, 10 and 15s. The etched crystal is shown in Figure 3.15(a)-(d). The surface morphology of the as grown crystal is shown in Figure 3.15(d). From the etching time of 5s (Figure 3.15(a)), some well-defined trapezoidal shape etch pits were formed. The size of etch pits is found to increase for higher etching times while the etch pits become more prominent and well defined etch patterns were obtained. (Figure 3.15(b)). These may be due to fluctuations in supersaturation at some points on the surface of the crystal during the growth process (Sangwal 1987). Figure 3.15(c) represents the identical elongated etch patterns observed on
the grown LHT crystal surface after 15s. From the etching studies, it is concluded that the LHT crystal has adopted layer-by-layer growth mechanism (Siva Shankar et al 2009).

3.4 Growth and Characterization of Sodium Hydrogen L-Tartrate Monohydrate Single Crystal

3.4.1 Experimental

3.4.1.1 Synthesis and Crystal Growth

AR grade materials were used for the synthesis of Sodium Hydrogen L-Tartrate Monohydrate (SHT) single crystal by slow evaporation technique. L-tartaric acid and sodium nitrate were taken in equimolar ratio and dissolved in deionized water under constant stirring for 4h. The obtained solution was filtered and allowed to evaporate at room temperature. Optically good quality crystal of dimension 1.2×0.4×0.2cm$^3$ was harvested in a span of 40 days which is shown in Figure 3.16. The crystal was further purified by the repeated recrystallization process. The chemical reaction involved in the formation of SHT crystal is given in Equation 3.18.

$$\text{C}_4\text{H}_6\text{O}_6 + \text{NaNO}_3 \rightarrow \text{NaH[Ca}_4\text{H}_4\text{O}_6\cdot\text{H}_2\text{O} + \text{HNO}_3} \quad (3.18)$$

L-tartaric acid  Sodium nitrate  SHT

<table>
<thead>
<tr>
<th>Crystal data</th>
<th>SHT</th>
</tr>
</thead>
<tbody>
<tr>
<td>Space group</td>
<td>P2$_1$/2$_1$2$_1$</td>
</tr>
<tr>
<td>Crystal System</td>
<td>Orthorhombic</td>
</tr>
<tr>
<td>a(Å)</td>
<td>7.22</td>
</tr>
<tr>
<td>b(Å)</td>
<td>8.66</td>
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<tr>
<td>c(Å)</td>
<td>10.58</td>
</tr>
<tr>
<td>Volume(Å$^3$)</td>
<td>662</td>
</tr>
</tbody>
</table>

Table 3.5 Crystallographic data of SHT

Figure 3.16 As grown crystal of SHT
3.5 Result and Discussion

3.5.1 Single Crystal X-ray Diffraction Analysis

The XRD data were collected using single crystal X-ray diffraction analysis. It is observed from the X-ray diffraction data that the SHT crystal is of orthorhombic structure with space group P2₁2₁2₁. The calculated lattice parameter values are tabulated in 3.5 and it agrees well with the reported values (Bott et al 1956, Kubozono et al 1993, Bott et al 1993).

3.5.2 Powder X-ray Diffraction Analysis

The powder X-ray diffraction study was carried out in the range of 10-70° using CuKα radiation to identify the reflection planes of the grown SHT crystals as shown in Figure 3.17. Two-theta values were taken as the input data for the calculation of (h k l) indices of the reflected planes using “Powder X” software. The sharp and intense peaks in the pattern confirm the high crystallinity and good quality of the grown crystal (Parasuraman et al 2011).

3.5.3 FTIR Studies

The functional groups present in the molecular structure of the SHT crystal are confirmed by Fourier transform infrared spectrum and it is shown in Figure 3.18. The peak
located at 1575 and 1404 cm\(^{-1}\) are attributed to asymmetric and symmetric vibrations of COO\(^-\) respectively (Yun Zhang et al 2007). The sharp peak observed at 1737 cm\(^{-1}\) indicates the presence of C=O (Martin Britto Dhas et al 2007). The peaks observed at 1132 and 1068 cm\(^{-1}\) represent the C-O stretching mode of tartaric acid (Manikandan and Dhanuskodi 2007, Urit Charoen-In et al 2015). The peak at 904 cm\(^{-1}\) reflects the C-C stretching mode (Suryanarayana and Dharmaprakash 2000). The \(-\text{OCH}\) stretching vibration is observed at 1306 cm\(^{-1}\) (Suryanarayana and Dharmaprakash 2000). The strong, broad, and multicomponent absorption extending into the region between 3319-2501 cm\(^{-1}\) indicates the existence of the weak hydrogen bonds (Yun Zhang et al 2007). The peaks at 842 and 574 cm\(^{-1}\) may be the absorption peak of the bonding between Na\(^+\) ion and the carbonyl group in the tartaric acid molecule (Urit Charoen-In et al 2015). The vibrational assignments of the grown crystal are well agreed with reported values (Urit Charoen-In et al 2015).

![Figure 3.18 FTIR spectrum of SHT](image)

**Figure 3.18 FTIR spectrum of SHT**

### 3.5.4 UV-vis-NIR Studies

The UV absorbance spectrum was recorded to know the suitability of the crystals for optical applications. The optical spectrum of SHT crystal were recorded in the frequency region 190-1100 nm as in Figure 3.19. It has wide transparency in the visible and IR region,
which is an essential requirement for NLO applications (Sreekanth et al 2012). The lower
cutoff wavelength of the crystal is at 235nm and the corresponding value of band gap energy
($E_g$) is estimated to be 5.3eV using the Equation 3.2.

3.5.5 Optical Constants Estimation

Optical band gap ($E_g$) of the material is an important requirement for linear and
nonlinear optical applications. According to the Tauc’s relation, the absorption coefficient $\alpha$
for a material is given by

$$\alpha \nu = B(\nu E_g)^m$$  \hspace{1cm} (3.19)

where $E_g$ is the band gap energy, $B$ is a constant which is different for different transitions, $\alpha$ 
is the optical absorption coefficient, $\nu$ is the energy of photon and $m$ is an index which
assumes the values 1/2 for direct allowed transition, 2 for indirect allowed transition, 3/2 for
direct forbidden transition, 3 for indirect forbidden transition depending upon the nature of
electronic transitions.

![Figure 3.19 UV-vis-NIR spectrum of SHT](image)

The optical absorption coefficient ($\alpha$) of SHT crystal at different wavelengths was calculated
using the relation (Robert et al 2010),

$$\alpha = \frac{2.3026 \log \left( \frac{I_0}{I} \right)}{t}$$  \hspace{1cm} (3.20)
where $T$ is the transmittance and $t$ is the thickness of the sample used for the optical absorption study. The plot of $(\alpha h\nu)^2$ versus $h\nu$ for direct transition (i.e. $m = 1/2$ in our case) is shown in Figure 3.20. Intercept of the linear portion of the plot on the $h\nu$ axis gives the value of direct band gap energy $E_g$ of the grown crystal and it is found to be 5.28eV which indicates the insulating nature of the crystals (Krishnan et al 2010). The larger optical band gap energy shows that the defect concentration in the grown crystal is very low (Parthasarathy et al 2012).

The refractive index of the optical material can be calculated using the transmission spectrum of the grown crystal. The reflectance of the crystal was found in terms of absorption coefficient using the relation (Kasap and Capper 2006, Robert et al 2010),

$$R = 1 \pm \frac{\sqrt{1-\exp(-\alpha t)+\exp(\alpha t)}}{1-\exp(-\alpha t)}$$  \hspace{1cm} (3.21)

$$n_1 = \frac{-(R+1)\pm\sqrt{-3R^2+10R-3}}{2(R-1)}$$  \hspace{1cm} (3.22)

The linear refractive index ($n_1$) was calculated in terms of reflectance given in Equation 3.21 and found to be in the transmission region of $n_1 = 2.62$. The optical studies reveal that the crystal possesses good optical behaviour for using it in device applications.

![Figure 3.20 Tauc's plot of SHT](image-url)
3.5.6 Fluorescence Studies

The fluorescence emission spectrum was recorded in the wavelength range from 270 to 480nm with excitation wavelength of 250nm as shown in Figure 3.21. A strong emission band was observed at 352nm. The spectrum indicates that SHT is efficient for absorption of ultraviolet light and emission of light in the near-ultraviolet band. Small bands observed in the visible region may be due to microscopic lattice defects, whereas high intensity and discrete nature of the major emission band indicates that the grown crystals are free from the major defects (Preeti Singh et al 2013). A strong emission at 352nm in the UV region makes SHT crystal applicable for luminescent devices (Rajendran and Gajendiran 2015).

![Fluorescence spectrum of SHT](image)

Figure 3.21 Fluorescence spectrum of SHT

3.5.7 SHG Studies

The Second Harmonic Generation (SHG) efficiency of the grown crystals was confirmed by Kurtz-Perry powder technique (Kurtz and Perry 1968) using Nd:YAG laser of wavelength 1064 nm, with an input power of 450mJ, a pulse width of 10ns and a repetition rate of 10Hz. The powdered SHT samples were loaded into uniform bore glass capillaries. The samples were exposed to laser radiation and the output from the sample was monochromated to collect the output intensity. The second harmonic signal generation of the
grown crystal was confirmed with the emission of green radiation. The output power of SHT crystal was compared with the standard KDP crystal by passing the same input energy through it and is about 0.3 times of KDP.

3.5.8 Thermal Studies

Thermal analyses were performed on the grown crystals to study the thermal stability and melting point. The TG/DTA analysis of SHT was carried out from room temperature to 600°C in the nitrogen atmosphere using NETZSCH STA 409 PC with the heating rate of 10°C/min. The powdered sample of 3.04mg of SHT was used for this analysis. The different stages of weight loss are clearly given in TGA and DTA traces as shown in Figure 3.22.

![Figure 3.22 TG/DTA analysis of SHT](image)

From the TGA spectrum, it is inferred that there is 10.45% weight loss owing to loss of water of crystallization. The major weight loss of 48.58% occurs between the temperatures 240-350°C is due to the decomposition of gaseous fragments like carbon monoxide, carbon dioxide and ammonia might be liberated from the thermal degradation of the compound associated with SHT (Arora et al 2005, Urit Charoen-In et al 2015). There is a gradual
decomposition of the SHT crystal from 280 to 600°C and giving a residue of 28.77%, which is mainly the sodium present in the crystal, since its boiling point is 883.1°C. From the DTA curve, there is a peak at 240°C, which is due to the melting of the material. The results of the DTA analysis are being consistent with the TGA data. It is observed that the compound is stable up to 240°C. There is no phase transition till the material melts and this enhances the temperature range for the utility of the crystal for NLO applications (Kirubavathi et al 2008).

Figure 3.23 Plot of 1/T vs Log [-Log (1-α)/T²] of SHT

Table 3.6 Kinetic parameters of SHT

<table>
<thead>
<tr>
<th>Kinetic parameters</th>
<th>values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Activation energy (E) in kJ mol⁻¹</td>
<td>-113.13</td>
</tr>
<tr>
<td>Frequency factor (A) in kS⁻¹</td>
<td>-11.02</td>
</tr>
<tr>
<td>Enthalpy of activation (ΔH) in kJ mol⁻¹</td>
<td>-229.86</td>
</tr>
<tr>
<td>Entropy of activation (ΔS) in J K⁻¹ mol⁻¹</td>
<td>122</td>
</tr>
<tr>
<td>Gibb’s free energy (ΔG) in kJ mol⁻¹</td>
<td>790.58</td>
</tr>
</tbody>
</table>

The kinetic parameters, namely activation energy (Eₐ), enthalpy (ΔH), entropy (ΔS) and Gibb’s free energy of activation (ΔG) were obtained from the first stage of decomposition by using Coats-Redfern relation given in Equation 3.3. The Plot of 1/T vs Log [-Log (1-α)/T²] of SHT is shown in Figure 3.23. The values of Eₐ, A, ΔS, ΔH and ΔG for the
first stage of decomposition of the crystal are calculated using Equations from 3.4 to 3.8 respectively (Krishnan et al 2013) and presented in Table 3.6. The activation energy ($E_a$) is negative, which reveals that the energy required to make the reaction is very less. The value of enthalpy ($\Delta H$) indicates the release of energy in the reaction. The Gibb’s free energy, $\Delta G<0$ proves that the reaction is nonspontaneous. The calculated values of kinetic parameters of SHT would be useful in gasification process.

### 3.5.9 Dielectric Studies

Dielectric constant and dielectric loss (tan $\delta$) values were found in the frequency range 50Hz to 5MHz. Dielectric studies were performed for temperatures 323, 333 and 343K with the crystal of dimension 7.25x2.48x1.68mm$^3$. The crystal was coated with conductive silver paint for metallic contacts. The dielectric constant of SHT was found by measuring the capacitance of the samples and calculating the dielectric constants assuming that each sample behaves like a parallel plate capacitor. From the data, the dielectric constant at each temperature is calculated using the Equation 3.9.

The variations of dielectric constant as a function of Log frequency for different temperatures are shown in Figure 3.24. It is found that the dielectric constant decreases with
increase in frequency and attains lower value at high frequencies. There are four types of polarizations occurred by applying an electric field over a material i.e., electronic, ionic, orientation and space charge polarization. At lower frequency, the polarization follows the alternation of the electric field, resulting in that the dielectric constant is independent of the frequency. At higher frequency, ionic polarization cannot follow the field variations and ceases, but the existence of electronic polarization results in low dielectric constant (Bhaskaran et al 2008). It is clear that the variation of dielectric constant with varying temperature is very less which suggests that the sample possesses high chemical homogeneity (Hiremath and Venkataraman 2003).

The dielectric loss is calculated using Equation 3.10 as shown in Figure 3.25. Dielectric loss also decreases with increasing the frequency. In the high frequency region, both the dielectric constant and dielectric loss attains almost constant values. A similar behaviour was observed for all the temperatures. Dielectric properties of SHT crystal shows that it is a potential material for fast switching times in electro-optic applications.

3.5.10 Mechanical Studies

In the microhardness studies, indentations were made on the sample using a Vicker’s pyramidal diamond indenter for various loads ranging from 25-100g and the indentation time was kept constant as 10s. The distance between any two consecutive indentations was kept at more than thrice the diagonal length of the indentation mark. Thus surface effects were independent of one another. Several impressions were made for each load and the diagonals (d) were averaged.

The Vicker’s hardness numbers (H_v) were calculated using the Equation 3.11. A graph was plotted between hardness number (H_v) and applied load P as shown in Figure 3.26. It is observed that the hardness increases with increase in load satisfying Reverse Indentation Size Effect (RISE) (Dhanuskodi et al 2011). A plot of Log P vs Log d is shown in Figure
3.27, fitting data before cracking gives a straight line (by least square fitting), which is in good agreement with Meyer’s law (Meyer 1908). The Meyer’s index, n is found using Equation 3.13 from the slope of the graph and the value is 3.47. Observations made by Onitsch (Onitch 1947), ‘n’ should lie between 1 and 1.6 for harder materials and above 1.6 for softer materials. Thus the SHT crystal belongs to soft material.

![Figure 3.26 Load (P) vs H, of SHT](image)

![Figure 3.27 Plot of Log P vs Log d H, of SHT](image)

![Figure 3.28 Plot of d^n vs d^2 of SHT](image)

The hardness parameters were calculated using Equation 3.15 by least square fitting of the plot d^n versus d^2 as shown in Figure 3.28 and the calculated values are given in Table

102
3.7. The mechanical properties like yield strength ($\sigma$), stiffness constant ($C_{11}$) of the SHT were calculated using the Equations 3.16 and 3.17 respectively (Revathi and Rajendran et al 2016) and are given in Table 3.8 indicates the strong binding forces between the ions of SHT.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>$n$</td>
<td>3.47</td>
</tr>
<tr>
<td>$K_1$ (Kg/m)</td>
<td>$2.3812 \times 10^2$</td>
</tr>
<tr>
<td>$K_2$ (Kg/m)</td>
<td>$7.6379 \times 10^4$</td>
</tr>
<tr>
<td>$W$ (m)</td>
<td>$3.6034 \times 10^4$</td>
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</table>

<table>
<thead>
<tr>
<th>Load P(g)</th>
<th>$C_{11}$ (GPa)</th>
<th>$\sigma_v$ (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>1.3067</td>
<td>1.5954</td>
</tr>
<tr>
<td>50</td>
<td>1.9025</td>
<td>2.0994</td>
</tr>
<tr>
<td>100</td>
<td>3.7959</td>
<td>2.7311</td>
</tr>
</tbody>
</table>