CHAPTER 3

GROWTH AND CHARACTERIZATION OF ORGANOMETALLIC NLO MATERIAL: CESIUM HYDROGEN TARTRATE

3.1 INTRODUCTION

Nonlinear optics (NLO) emerged nearly five decades ago with the development of the first operating laser and the demonstration of frequency doubling phenomena. The extraordinary growth and development of nonlinear optical materials has rendered as an indispensable part of different applications. With the emerging demand, nonlinear optical materials have been considered as the key elements for the photonic technologies like optical computing, telecommunications, optical interconnects, high density data storage, sensors, image processing, switching, etc. Organic materials are formed by weak Van der Waals and hydrogen bonds and hence possess a high degree of delocalization. The advantages of organic materials include ease of varied synthesis, scope for altering the properties by functional substitutions, inherently high nonlinearity and high damage resistance, etc.

The inorganic materials are much more matured in their application to second order NLO materials than its counterpart with the following characteristics: a wide optical transparency domain, high laser damage threshold, and large nonlinear figure of merit, wide phase matchable angle, ease of fabrication, thermal stability, high mechanical strength and fast optical response time. Semi organic nonlinear optical crystals have imposed a new approach in the field of second harmonic generation. They have combined properties of both organic and inorganic crystals which make them suitable
for the fabrication of devices. The semi-organic crystals attract great attention in the field of nonlinear optics due to their optical nonlinearity, chemical flexibility, thermal stability and excellent transmittance in the UV–visible region. The semi-organic crystals possess properties such as high damage threshold, wide transparency region and high nonlinear coefficient, which have various applications and they need NLO require single crystals in the bulk form. This is achieved with the crystals, which exhibit wide transparency, large and bulky crystal morphologies.

The Organometallic compounds contain metal and organic ligands linked by coordination bond. These types of complexes are much interest in the field of optical fabrication. The structure of the organometallic compound can be varied by changing the metal, co-ordination number and ligands. Compounds of tartaric acid have a variety of practical applications in science and technology. Tartaric acid crystals are used for nonlinear optical devices based on their optical second harmonic generation; optical transmission characteristics. A number of tartaric acid based NLO complexes are reported earlier. Most of the Tartrate based inorganic crystals such Barium Tartrate, Strontium and Rubidium Tartrate, Yttrium Tartrate, Samarium Tartrate, Calcium Tartrate and Zinc Tartrate have much more interest based on their optical Second Harmonic Generation (SHG), optical transmission characteristic, fabrication of crystal oscillators and resonators, controlled laser emissions and they are identified for pyro-electric, piezoelectric, dielectric and ferroelectric transitions.

Among the several tartrate compounds, Cesium Hydrogen Tartrate has received greater attention on account of its spectral characteristics. In the present work, non-aromatic organic tartaric acid and inorganic Cesium Chloride are mixed to get organometallic Cesium hydrogen Tartrate single crystal (CT). Due to the proton ionization, the hydrogen atom in tartaric acid
is easily removed and it is replaced by Cs\(^+\) ions to form the Cesium Tartrate single crystal.

During the past few years, Perovskite solar cells have experienced an unprecedented rapid development in the power conversion efficiency (PCE) and the record PCE has been already comparable to the traditional polycrystalline silicon solar cells. The cesium (Cs)-doped perovskites show more superior stability for the future commercial application. Here, recent progress of the inorganic cesium application in organic -inorganic perovskite solar cells (PSCs) is highlighted from the device efficiency and for device stability. Now a day, researcher has shown more interest in perovkites doped crystal such as cesium chloride doped L-threonine, Cesium - Doped L - Asparaginone Crystals cesium-based tin perovskites (CsSnI\(_3\)) Enhanced UV-light stability of planar heterojunction perovskite solar cells with cesium bromide interface modification,etc., to provide the high efficiency with more device stability.

The single crystals of CT were grown by the slow evaporation solution growth technique and the grown crystals of CT is characterized via Powder X-ray diffraction (PXRD), Fourier Transform Infrared (FT-IR), Fourier Transform Raman (FT-RAMAN), Thermogravimetric (TG/DTA), Second Harmonic Generation (SHG), Vicker’s Microhardness, UV-Vis-NIR studies, Dielectric and Etching studies.

3.2 EXPERIMENTAL PROCEDURES

3.2.1 Material Synthesis and Crystal Growth

The good quality NLO crystals of Cesium Hydrogen Tartrate were grown by slow evaporation solution growth technique. Chemicals used for the growth of CT crystals were Cesium Chloride (CsCl) and L-Tartaric acid (C\(_4\)H\(_6\)O\(_6\)). Compounds were taken in the molar ratio of 1:1 and dissolved in
the ethanol solvent separately. Then the solution was mixed together and stirred continuously for 3 hours using a magnetic stirrer. After ensuring the homogeneity and maintaining the pH value of the solution as 4, the solution was filtered using Whatman grade one filter paper to remove the suspended impurities. A constant pH of 4 is maintained for this solution. The clear filtrate so obtained was kept inside unperturbed dust free atmosphere for the growth of CT crystals at the room temperature. Well-defined, colorless and transparent single crystals of CT were collected after 30 days. The as grown CT crystals are shown in Figure 3.1.

![Figure 3.1 Grown crystals of CT crystal](image.png)

### 3.2.2 Characterization Techniques

The Powder X-ray diffraction (PXRD) data of CT crystal were collected using XPERT-PRO X-ray diffractometric systems. The XRD pattern was used to determine the cell parameters of the CT crystal.
The FT-IR spectrum of CT crystal was recorded in the wave number range 400 - 4000 cm\(^{-1}\) using SHIMADZU FT-IR spectrometer. The FT-Raman spectrum of CT crystal was recorded in the frequency range 4000 - 400 cm\(^{-1}\) using BRUKKER RFS27 FT-Raman spectrometer. The FT-IR and FT-Raman spectral analysis were used to confirm the presence of various functional groups in the CT crystal. TG/DTA analysis of Cesium Hydrogen Tartrate crystals were carried out by using a NETZSCH STA 449F3 thermal analyzer between room temperature and 500\(^{\circ}\)C at a heating rate of 10 \(^{\circ}\)C in the atmosphere of nitrogen gas. The Vicker’s microhardness of the CT crystal was measured using HMV SHIMADZU microhardness tester with load ranging from 1 to 25g. The second order nonlinear optical (NLO) property of the CT crystal was confirmed by the modified Kurtz-Perry technique. The Q-switched Nd: YAG laser of wavelength 1064 nm with an input power of 5.7 mJ and pulse width of 8ns with a repetition rate of 10Hz was used in the technique.

The UV-Visible absorption spectrum of CT crystal was recorded using Perkin Elmer Lamda 35 spectrophotometer in the spectral range 200 to 1200nm. Dielectric studies were carried out on the grown CT crystal using an LCR meter at various frequencies in the range from 50Hz to 5MHz and at different temperatures ranging from 333 K, 343 K, 353 K and 363 K. Etching study was also carried out for the CT crystal on (100) plane with water as an etchant. The detailed reports of the above analysis are presented in the preceding sections.

3.3 RESULTS AND DISCUSSION

3.3.1 Powder X-ray Diffraction Analysis

The simulated and experimental powder XRD pattern of CT crystal is shown in Figure 3.2. The cell parameter values for CT crystal were also obtained from Powder XRD patterns which indexed by using XRDA
software. It found that Cesium Hydrogen tartrate crystals are grown in orthorhombic crystal system with noncentrosymmetric space group of \( P2_12_12_1 \) and lattice parameters are \( a=8.0855 \, \text{Å}; \, b=11.6698 \, \text{Å}; \, c=7.6289 \, \text{Å}; \, V=719.833 \, \text{Å}^3 \). The parameters obtained by powder XRD analysis are in close agreement with the reported values (Lieselotte et al. 1978). Table 3.1 gives the calculated cell parameters values.

Figure 3.2 Powdered XRD pattern of CT crystal: (a) simulated and (b) experimental
Table 3.1  The cell parameter, cell volume and crystal system of CT crystal

<table>
<thead>
<tr>
<th>Category</th>
<th>Crystal system</th>
<th>Space group</th>
<th>Volume (Å³)</th>
<th>Cell parameters (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reported value</td>
<td>Orthorhombic</td>
<td>P2₁2₁2₁</td>
<td>V=719.823</td>
<td>a = 8.076 (3)</td>
</tr>
<tr>
<td>(Lieselotte et al. 1978)</td>
<td></td>
<td></td>
<td></td>
<td>b = 11.621 (5)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>c = 7.692  (3)</td>
</tr>
</tbody>
</table>

| Obtained value       | Orthorhombic   | P2₁2₁2₁     | V=719.833   | a= 8.0855 (3)       |
|                      |                |             |             | b = 11.6698(5)      |
|                      |                |             |             | c = 7.6289(3)       |

### 3.3.2 FT-IR and FT-Raman Spectroscopic Analysis

The FT-IR and FT-Raman spectra of the CT crystal are presented in the Figure 3.3 and Figure 3.4. The OH stretching vibrations is generally appeared as broadband between 3700cm⁻¹ and 2400cm⁻¹. The presence of OH stretches confirms the O-H…O intermolecular hydrogen bonding the titled compound. The vibrational stretch observed at 3321 cm⁻¹ in the FT-IR and 3355 cm⁻¹ in the FT-Raman spectrum are assigned to O-H stretching vibrations with H-bonded. The presence of intermolecular hydrogen bond is responsible for SHG behavior in CT. Bands at 2953 cm⁻¹, 2723 cm⁻¹ and 2509 cm⁻¹ in FT-IR spectrum and its counterpart FT-Raman bands observed at 2970 cm⁻¹, 2929 cm⁻¹ and 2886cm⁻¹ are assigned to C-H stretching vibration. The carbonyl group exhibits a strong absorption band due to C=O stretching observed in the region 1850-1550 cm⁻¹. The vibrational peak appeared at 1735 cm⁻¹ in FT-IR and 1713 cm⁻¹ in FT-Raman are assigned as C=O stretching vibration. Salt of carboxylic acids has a very strong and characteristic peak in the region 1695-1540 cm⁻¹ due to the asymmetric stretching vibrations of CO₂⁻. The peaks appeared at 1566 cm⁻¹ in FT-IR and 1538 cm⁻¹ in FT-Raman is attributed to the antisymmetric stretching of the carbonyl group.
Figure 3.3 FTIR spectrum for CT Crystal

Figure 3.4 FT-Raman spectrum for CT Crystal
The symmetric stretching vibration of this group gives rise to a band at 1406 cm\(^{-1}\) in FT-IR and the band at 1366 cm\(^{-1}\) in FT-Raman. The peak at 1060 cm\(^{-1}\) in FT-IR and at 1077 cm\(^{-1}\) in FT-Raman may be assigned to out of plane deformation of O-H and C-O bending. The absorption peaks absorbed at 792 cm\(^{-1}\) in FT-IR and at 786 cm\(^{-1}\) in FT-Raman, due to C-H bending (out of plane) and O-H bending (out of plane). The bands at 540 cm\(^{-1}\) in FT-IR and 519 cm\(^{-1}\) in FT-Raman is due to C-C=O bending due to metal oxygen bonding (cesium-oxygen). The FT-IR and FT-Raman bands are summarized in Table 3.2.

**Table 3.2**  Wave number of absorption peaks in FT-IR and FT-Raman spectrums and their assignments of CT Crystals

<table>
<thead>
<tr>
<th>Frequency in cm(^{-1})</th>
<th>Assignments</th>
</tr>
</thead>
<tbody>
<tr>
<td>FT-IR</td>
<td>FT-RAMAN</td>
</tr>
<tr>
<td>3321</td>
<td>3355</td>
</tr>
<tr>
<td>2509, 2723, 2953</td>
<td>2970, 2929, 2886</td>
</tr>
<tr>
<td>1735</td>
<td>1713</td>
</tr>
<tr>
<td>1566</td>
<td>1538</td>
</tr>
<tr>
<td>1406</td>
<td>1366</td>
</tr>
<tr>
<td>1060</td>
<td>1077</td>
</tr>
<tr>
<td>792</td>
<td>786</td>
</tr>
<tr>
<td>580</td>
<td>519</td>
</tr>
</tbody>
</table>
3.3.3 Thermal Analysis

Thermal stability of the grown crystal was carried out using NETZSCH STA 449F3 thermal analyzer between room temperature and 500 °C at a heating rate of 10 °C in the atmosphere of nitrogen gas. In TG curve, it is observed that there is no major weight loss absorbed below 234°C, decomposition of the material starts from 234°C and the second stage decomposition occurs between 255 °C and 313 °C, it may be due to elimination of carbon dioxide molecules. There is no considerable change of weight-loss of the material noticed above 313 °C. In DTA, there is no endothermic and exothermic trace before 100°C which reveals that there is no water molecule in this compound, An endothermic is observed at 234 °C may due to the melting point of the CT crystal and ascertain the suitability in NLO applications up to 234 °C.

![Figure 3.5 DTA of CT Crystal](image-url)
The good degree of crystallinity of the sample is revealed from the sharpness of the endothermic peak. The Figure 3.5 shows the TG/DTA plot of CT crystal.

### 3.3.4 Vicker’s Microhardness Test

Mechanical stability of the CT crystals was analyzed by the Vicker’s microhardness tester. The Vicker’s hardness is obtained by the following relations $H_V = 1.8544 \frac{P}{d^2}$, Where, $H_V$ is the Vicker’s hardness number, $P$ is the applied load in kg and $d$ is the arithmetic mean length of the two diagonals. Figure 3.6 shows the variation of Hardness ($H_V$) as a function of applied loads.

From the plot, it found that $H_V$ increases with an increase in the applied load ranging from 1 to 25g of CT crystal. Vicker’s microhardness number increase with increase in load is known as reverse indentation size effect and beyond 25g the crack and fragmentation were observed in the CT crystals. The Meyer’s index number was calculated from the Meyer’s law

$$P = k \, d^n$$  \hspace{1cm} (3.1)

Where, $k$ is the material constant and $n$ is the Meyer’s index (or work-hardening coefficient). Hence $\log P = \log k + n \log d$. The value of ‘n’ is determined from the plot between $\log P$ and $\log d$, $H_V$ increases with the increase of $P$ if $n > 2$ and decreases with increase of $P$ when $n < 2$. The value of ‘n’ is determined from the plot between $\log P$ and $\log d$ as shown in Figure 3.7. From the plot, the work hardening index (n) which is found to be 2.313.
Figure 3.6 Variation of Load with Hardness of CT Crystal

Figure 3.7 Variation of Log D with Log P for CT Crystal
According to Hanneman, the value of ‘n’ is less than 2 for hard materials and more than 2 for soft ones. Thus the CT crystal belongs to the soft category material. The Elastic stiffness constant ($C_{11}$) of CT crystal was calculated using Wooster’s empirical relation which provides information about the binding force present between the molecule. The CT crystal has large value of mechanical strength and it was established that this material could be suitable for device fabrications. The calculated stiffness constant for different loads were tabulated in Table 3.3.

Table 3.3 Elastic stiffness constant for CT crystals

<table>
<thead>
<tr>
<th>Sl. No</th>
<th>Load ($10^3$kg)</th>
<th>Hardness Values (Hv) kg/mm$^2$</th>
<th>$C_{11} \times 10^{14}$ Pa</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>7.4</td>
<td>0.33</td>
</tr>
<tr>
<td>2</td>
<td>3</td>
<td>9.7</td>
<td>0.53</td>
</tr>
<tr>
<td>3</td>
<td>5</td>
<td>15.2</td>
<td>1.17</td>
</tr>
<tr>
<td>4</td>
<td>10</td>
<td>22.4</td>
<td>2.31</td>
</tr>
<tr>
<td>5</td>
<td>25</td>
<td>31.8</td>
<td>4.26</td>
</tr>
</tbody>
</table>

3.3.5 NLO Test – Kurtz Powder SHG Method for CT Crystal

The relative SHG efficiency of the CT crystal is determined by Kurtz and Perry technique. The NLO property of the sample was tested using a Q-switched Nd: YAG laser beam of wavelength 1064nm and 8ns pulse width with an input rate of 10Hz. The output of the grown crystal was measured as 13mV while the KDP gave an SHG signal of 9mV for input beam energy of 5.7 mJ/ Pulse. The green radiation generated confirms the second harmonic signal in the crystalline sample. The standard NLO inorganic KDP was used as the reference material. The emission of green light ($\lambda=532$ nm) from the CT crystals confirmed their non-centrosymmetric crystal structure. This tendency of the CT crystal may be due to the presence
of the cesium ions and unionized tartaric acid, which are stabilized by strong intermolecular interactions between the molecules present in the CT crystal. Thus, the SHG efficiency of CT crystal was found to be 1.5 times greater than KDP crystal.

### 3.3.6 UV-Visible Studies

The transparency of the crystal plays an important role in the field of optical fabrication and optical signal processing. The good transparency of the crystal in the entire visible region suggests its suitability for SHG efficiency applications. Figure 3.8 represents the absorbance spectrum of grown CT crystal was recorded in the wavelength region from 200 nm to 1200 nm. It is inferred that the observed wide transmission in the lower cutoff wavelength at 253 nm enables it to be a potential candidate for optoelectronic and it is the most desirous properties of materials possessing NLO activity.

![Figure 3.8 UV-Vis Absorption spectrum of CT Crystal](image.png)
3.3.7 Dielectric Characterization

Dielectric studies furnish a great deal of information about perfection, crystal structure and chemical composition. A study of the dielectric properties of solids gives information about the electric field distribution within the solid. The action of an electric field brings the charges of the molecules of the dielectric into a certain ordered arrangement in space. The study of dielectric constant of a material gives an insight into the nature of bonding in the material. Defect-free and transparent crystal was selected and used for the dielectric measurement. The capacitance and dissipation factor of the sample were measured for various frequencies, in the range 50 Hz to 5 MHz.

The relative dielectric constant $\varepsilon_r$ is

$$\varepsilon_r = \frac{Cd}{A\varepsilon_0}$$

(3.2)

Where, $C$ is the capacitance, $d$ is the thickness of the crystal, $\varepsilon_0$ is the free space permittivity and $A$ is the area of the crystal. The plot of dielectric constant vs. frequency of the CT crystal at different temperatures 333 K, 343 K, 353 K and 363 K are shown in Figure 3.9. The dielectric constant has high values in the lower frequency region and decreases with an increase in frequency. In accordance with Miller rule, the lower value of dielectric constant is a suitable parameter for the enhancement of SHG efficiency. The variation of $\varepsilon_r$ with temperature is generally attributed to the crystal expansion, the electronic and ionic polarizations and the presence of impurities and crystal defects. The low value of dielectric constant at high frequencies indicates the low power dissipation and that the crystal can be highly suitable for electro-optic applications. The dielectric loss very much depends on temperature and frequency.
The dielectric loss also depends on frequency of the applied field like dielectric constant. The plot of dielectric loss vs. frequency of the CT crystal at temperatures 333 K, 343 K, 353 K and 363 K are shown in Figure 3.10. The dielectric loss which is low at high frequencies reveals that the CT crystal is of good quality with lesser defects. The dielectric constant and dielectric loss of the CT crystal increases with temperatures for a constant frequency due to the contribution of number of dipoles and weakening of inter force between the dipoles. The alternating current conductivity is calculated using the relation

\[ \sigma_{ac} = \omega \varepsilon_0 \varepsilon_r \tan \delta, \] (3.3)

Where \( \omega \) is the angular frequency, \( \omega = 2\pi f \), \( f \) is the frequency, \( \varepsilon_0 \) is the permittivity of the free space, \( \varepsilon_0 = 8.854 \times 10^{-12} \) Faraday per meter, \( \varepsilon_r \tan \delta \) are relative permittivity and dielectric loss respectively at a frequency (f). The plot of A.C. conductivity against frequency of CT single crystal is shown in Figure 3.11. The A.C. conductivity increases at higher frequencies region for temperature 353 K. It is observed that conductivity becomes independent of frequency. At low frequencies, random diffusion of charge carriers via hopping gives rise to a frequency independent conductivity on CT crystal.

The electronic exchange of the number of ions in the CT crystal gives the local displacement of electrons in the direction of the applied field, which in turn gives rise to polarization.
Figure 3.9 Dielectric Constant vs. frequency of CT Crystal

Figure 3.10 Dielectric loss vs. frequency of CT Crystal
Figure 3.11 A.C. conductance vs. frequency of CT Crystal

3.3.8 Chemical Etching Technique

The structural perfection of the CT crystal was studied by chemical etching technique and visualizes the dislocations in the single crystal. Etch pits are formed in the dislocation centers on the surface of the faces where the chemical complexes are present in the solution. In our present study, the etching was carried out on CT single crystal as to know the symmetry of the crystal from the shape and size of the etch pits. Figure 3.12 (a) and 3.12 (b) shows that different face of the CT crystal without water etchant. The linear layered etch pits without water etchant captured on the surface of the crystal due to reduced dislocations density. The surface etchant taken in time intervals of 30 and 60 seconds on CT crystal and it is cleaned gently using tissue papers. Then the etched patterns of CT crystal were photographed and it’s shown in the Figure 3.13 and Figure 3.14. It was found that the etch pits has slightly disappears on the faces where the additives are bounded, this gives the dislocations on the CT crystal. From these recorded etching patterns,
the possible reasons for large size etch pits in CT crystal may be due to the crystalline perfection.

Figure 3.12 (a) Etching study of CT Crystal without water etchant

Figure 3.12 (b) Etching study of CT Crystal without water etchant
Figure 3.13 Etching study of CT Crystal with water etchant for 30 seconds

Figure 3.14 Etching study of CT Crystal with water etchant for 60 seconds
3.3.9 Conclusion

Good optical quality NLO single crystals of CT were grown by slow evaporation solution growth technique. The crystal parameters and crystal system of the CT crystal is obtained from the powder X-ray diffraction technique and the values hold well with the reported values. The vibrational frequencies from FT-IR and FT-Raman spectral analyses confirms the presence of functional groups in the cesium tartrate material. The thermal studies confirm the thermal stability up to 234 °C. The Second harmonic efficiency of the crystal was found to be 1.5 times to the KDP. The micro hardness study confirms the mechanical strength of the layers of the sample. Thus, the increase of micro hardness with load is in good agreement with the reverse indentation size effect and the materials belong to soft materials. The lower cut off wavelength of the grown crystal at about 253 nm makes the material is suitable for UV filters.

From Dielectric studies it is found that the dielectric constant and dielectric loss of the CT crystal is high for low frequency region by subjecting temperature of 300 K. The increase in conductivity with the increase of frequency will be due to reduction in space charge polarization at higher frequencies. From these observed etching patterns, the possible reasons for large size etch pits in CT crystal is due to the crystalline perfection. When the crystal is etched in an etchant, the etch pits occurred more quickly in the less impurity content region.