CHAPTER 2

GROWTH, STRUCTURAL, OPTICAL AND THERMAL PROPERTIES OF DIAQUA (THIOCYANATO) MANGANESE MERCURY–N,N-DIMETHYLACETAMIDE SINGLE CRYSTALS

2.1 INTRODUCTION

Eventhough lot of potential nonlinear optical crystals are available, the search for new NLO crystals with enhanced performance has been progressing continuously. The recent research activities focus mainly on materials exhibiting excellent second order nonlinear optical (SONLO) properties because of their potential applications in optoelectronic technologies, telecommunication, computer and optical signal processing (Long 1995 and Nalwa 1991). Growth of metal-organic single crystals is much more important because they possess high physico-chemical stability, large NLO efficiency, non-hygroscopic nature and high optical damage threshold compared to organic and inorganic single crystals. In addition, presence of charge transfer in organometallics (metal to ligand and vice versa) enhances the hyperpolarizibility essential for NLO properties.

Recently, NLO materials with the tendency of the generation of blue violet light are more interesting for the specific applications. A series of bimetallic thiocyanates with general formula AB(SCN)₄ are found to possess promising nonlinear optical properties for the generation of blue violet light by frequency doubling of diode laser (Wang et al 2003a and Zhang et al
Manganese mercury thiocyanate (MMTC) has been reported as a potential nonlinear optical crystal among the bimetallic thiocyanate series, which shows higher powder second harmonic intensity compared to Urea (Wang et al 2001b). MMTC belongs to tetragonal structure with noncentrosymmetric I4 space group. Growth of good quality MMTC bulk single crystal is more difficult because of its very high solubility in aqueous medium and acetone-water mixed solvent and hence different additives like, dimethylacetamide (DMA) (Wang et al 2000a and 2002a), dimethylsulfoxide (DMSO) (Wang et al 2000b), N-methylpyrrolidone (NMP) (Wang et al 2002b) and glycol monomethyl ether (GME) (Wang et al 2002c) were introduced into MnHg(SCN)₄ and many new NLO materials were prepared with better NLO efficiency.

It has been reported that the interaction of dimethylacetamide (DMA) with MMTC forms a new complex of Diaqua (Thiocyanato) Manganese Mercury–N, N-dimethylacetamide (MMTWD), which possesses good stability and lower cut-off wavelength compared to MMTC. MMTWD belongs to three dimensional network systems (Wang et al 2000a). In MMTWD, two DMA molecules are not coordinated directly to any metal atoms, but involved in hydrogen bonding by acting as hydrogen-bond acceptors. The two water molecules coordinated directly to metal atoms by acting as hydrogen-bond donors. Such special structural features of the crystal result in better characteristics than those of MMTC. In the crystal structure of MMTWD, the deformed MnN₄O₂ octahedra, HgS₄ tetrahedra and thiocyanate ions create microscopic hyperpolarizibility, which inturn enhances the nonlinear optical property. The SHG efficiency of MMTWD was found to be higher than that of MMTWMP. The low value of specific heat capacity of MMTWD at room temperature (0.6930 J/g/K) makes the material suitable for applications with good phase matching ability. The growth and characterization of MMTWD single crystal has already been reported (Wang
et al 2003b). In the present investigation, the growth parameters have been optimized to grow bulk crystals of MMTWD with improved quality. The characterization studies such as CHN analysis to confirm the quality of the synthesized product, single crystal XRD, FTIR, laser Raman spectroscopy, linear and nonlinear optical properties, thermal properties, dielectric and etching studies have also been performed and the results are discussed in detail.

2.2 SYNTHESIS AND BULK CRYSTAL GROWTH OF MMTWD

2.2.1 Synthesis

High purity MMTWD was synthesized by two step reaction process. In the first step, manganese mercury tetra thiocyanate (MMTC) was synthesized based on the following reaction using E-Merck (99%) ammonium thiocynate (NH$_4$SCN), mercuric chloride (HgCl$_2$) and manganese chloride (MnCl$_2$) as basic reactants in deionized water.

$$4\text{NH}_4\text{SCN} + \text{HgCl}_2 + \text{MnCl}_2 \rightarrow \text{MnHg (SCN)}_4 + 4\text{NH}_4\text{Cl} \quad (2.1)$$

The resultant compound was recrystallised using hot water so that the coprecipitated NH$_4$Cl gets dissolved. The compound obtained through the above reaction was subjected to repeated recrystallization process using acetone – water (5:1). In the second step, powdered compound of this purified salt was used for the synthesis of Diaqua (Thiocyanato) Manganese Mercury – N,N-dimethylacetamide (MMTWD) as per the following reaction in deionized water.

$$\text{MnHg(SCN)}_4 + 2(\text{CH}_3)_2\text{N-CO-CH}_3 \rightarrow [\text{MnHg (SCN)}_4 (\text{H}_2\text{O})_2][(\text{CH}_3)_2\text{N-COCH}_3]_2 \quad (2.2)$$
Initially the calculated amount of DMA was diluted with deionized water and MMTC was added to this solution. Immediately MMTWD gets precipitated. Precipitated MMTWD was further recrystallised twice using water-DMA (1:1) mixed solvent. Purity of the synthesized product was analyzed by CHN test using Perkin-Elmer Series II 2400 CHNS/O Elemental Analyzer and the results are presented in Table 2.1.

**Table 2.1  CHN analysis of MMTWD compound**

<table>
<thead>
<tr>
<th>Element</th>
<th>Observed value (%)</th>
<th>Theoretical value (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>20.17</td>
<td>20.63</td>
</tr>
<tr>
<td>H</td>
<td>2.77</td>
<td>3.11</td>
</tr>
<tr>
<td>N</td>
<td>12.99</td>
<td>12.03</td>
</tr>
</tbody>
</table>

2.2.2  Solubility Studies of MMTWD

The purified MMTWD was finely powdered and used for the solubility study. In solution growth technique, the solubility of material in a given solvent plays a vital role in growing large size single crystals. Solubility studies were carried out in the mixed solvent of water-DMA (1:1) by gravimetric method for various temperatures. The recrystallised salt of MMTWD was added in small quantity to 100 ml of water-DMA (1:1) at 30°C by stirring the solution continuously. After attaining saturation, the equilibrium concentration of the solute was analyzed gravimetrically. The procedure was repeated for other temperatures like, 35, 40 and 45°C and the solubility was determined and plotted as shown in Figure 2.1.
2.2.3 Bulk Growth of MMTWD

Saturated solution of MMTWD was prepared based on the of solubility data. The seed crystals were obtained by spontaneous nucleation method using a mixed solvent of water-dimethyl acetamide (1:1) by slow evaporation method. Good quality MMTWD single crystal was selected as a seed crystal for the bulk growth experiment. Bulk crystal was grown from 300 ml saturated solution of MMTWD at 40°C in a constant temperature bath. Growth was initiated by reducing the solution temperature 0.01°C-0.1°C per day. Bulk crystal of dimension 1.6×1.3×1.4 cm³ was harvested after a typical growth period of 35 days. The threading of seed crystal induced some strain during the growth of MMTWD single crystals by slow cooling method. In slow evaporation method the saturated solution was kept at 42°C in a constant temperature bath. Good quality plate like crystal was obtained after 20 days. Crystals of MMTWD grown by slow cooling and evaporation methods and their corresponding morphology are shown in Figure 2.2(a), (b) and (c) respectively.
As grown crystals of MMTWD by a) slow cooling method b) slow evaporation method and c) Morphology of MMTWD single crystal

2.3 CHARACTERIZATION STUDIES

2.3.1 Single Crystal X-Ray Diffraction Analysis

The cell parameters and morphology of the MMTWD single crystal were determined by single crystal XRD analysis using Enraf-Nonius CAD4-MV31 X-ray diffractometer. MMTWD single crystal belongs to the tetragonal structure with P\(\bar{4}\) space group. The estimated lattice parameter values are a=12.2496 (4) Å, c=8.0719 (6) Å and V=1211.19(10) Å\(^3\) and are tabulated in Table 2.2. From the morphological studies, it is clearly observed that crystals grown by slow cooling method possess uniform growth rate along the three axes, whereas crystals obtained by slow evaporation method are generally
platy in habit. The facet containing (001) and (010) planes gets contracted with prominent (100) plane for the crystals grown by slow evaporation method. In the crystal structure of MMTWD, the two dimethyl acetamide (DMA) molecules are not coordinated to any metal atoms directly, but are involved in hydrogen bonding acting as hydrogen-bond acceptors with two coordinated water molecules acting as hydrogen-bond donors. Such special structural features of the new crystal result in better characteristics than those of MMTC, such as easy crystal growth and shorter cut-off wavelength.

Table 2.2 Crystal data of MMTWD single crystal

<table>
<thead>
<tr>
<th>Molecular formula</th>
<th>C\textsubscript{12} H\textsubscript{22} Mn Hg N\textsubscript{6} O\textsubscript{4} S\textsubscript{4}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular weight</td>
<td>698.17</td>
</tr>
<tr>
<td>Crystal structure</td>
<td>Tetragonal</td>
</tr>
<tr>
<td>Space group</td>
<td>(P\bar{4})</td>
</tr>
<tr>
<td>Unit cell parameters</td>
<td>(a=12.2496 \ (4) \ \text{Å},) (c=8.0719 \ (6) \ \text{Å}) (\alpha = \beta = \gamma = 90^\circ)</td>
</tr>
<tr>
<td>Formula unit (Z)</td>
<td>2</td>
</tr>
<tr>
<td>Cell volume (V)</td>
<td>(V=1211.19 \ (10) \ \text{Å}^3)</td>
</tr>
<tr>
<td>Density</td>
<td>1.916 Mg/m\textsuperscript{3}</td>
</tr>
</tbody>
</table>

The coordination of thiocyanate, N,N-dimethyl acetamide and water molecule can be explained based on the MMTWD crystal structure shown in the Figure 2.3. According to the HSAB concept, hard Mn\textsuperscript{2+} is coordinated with the harder nitrogen atom of thiocyanate (SCN) and oxygen atom of water (H\textsubscript{2}O) molecule. The soft Hg\textsuperscript{2+} is coordinated by the softer thiocyanate (SCN) sulfur atom. In this structure, the Mn\textsuperscript{2+} is hexa-coordinated with octahedral geometry. The four N atoms of (SCN) are coordinated
equatorially, and two water molecules combine axially with manganese (Mn) along the c axis to form MnN₄O₂ octahedra. The four sulfur atoms of the thiocyanate are coordinated with mercury atom to form HgS₄ tetrahedra, which in turn forms an infinite three-dimensional network system. The macroscopic non-linear susceptibility of MMTWD may be related to microscopic hyperpolarizabilities of the dipolar SCN ions and the deformed MnN₄O₂ octahedra and HgS₄ tetrahedra. Such a new special infinite three-dimensional network donates a large polarization, which in turn, induces a great macroscopic non-linearity (Wang et al 2000a).

Figure 2.3 Crystal structure of MMTWD viewed along c-axis
2.3.2 Powder X-Ray Diffraction Analysis

The crystallinity of the MMTWD crystal was confirmed by X-ray powder diffraction analysis using a Rich Siefert X-ray diffractometer. The finely crushed crystal powder was subjected to high intense X-rays of wavelength 1.5418 Å (CuKα) at a scan rate of 1°/minute. The completely indexed X-ray diffraction pattern of MMTWD is shown in the Figure 2.4. The differences in amplitude of the peak can be attributed to the difference in grain size and orientation of the powdered grains of MMTWD crystal. The lattice parameter values estimated from powder XRD coincide with the single crystal XRD results.

Figure 2.4 Powder X-ray diffraction pattern of MMTWD single crystal
2.3.3 High Resolution X-Ray Diffraction Analysis (HRXRD)

A multicrystal X-ray diffractometer was used to study the crystalline perfection of the single crystal (Lal and Bhagavannarayana 1989). Figure 2.5 shows the schematic diagram of the multicrystal X-ray diffractometer. The divergence of the X-ray beam emerging from a fine focus X-ray tube (Philips X-ray Generator; 0.4 mm × 8 mm; 2kWMo) is first reduced by a long collimator fitted with a pair of fine slit assemblies. This collimated beam is diffracted twice by two (Bonse and Hart 1965) types of monochromator crystals and thus the diffracted beam contains well resolved MoKα₁ and MoKα₂ components.

![Schematic diagram of Multi crystal X-ray diffractometer](image)

**Figure 2.5 Schematic diagram of Multi crystal X-ray diffractometer**

The MoKα₁ beam is isolated with the help of fine slit arrangement and allowed to further diffract from a third (111) Si monochromator crystal set in the dispersive geometry (+, -, -). Due to the dispersive configuration, though the lattice constant of the monochromator crystal and the specimen are different, the dispersion broadening in the diffraction curve of the specimen does not arise. Such arrangement disperses the divergent part of the MoKα₁...
beam away from the Bragg diffraction peak and there by gives a good collimated and monochromatic MoKα₁ beam at the Bragg diffraction angle, which is used as incident or exploring beam for the specimen crystal. The dispersion phenomenon is well described by comparing the diffraction curves recorded in dispersive (+,-,-) and non-dispersive (+,-,+) configurations. This arrangement improves the spectral purity (Δλ/λ << 10⁻⁵) of the MoKα₁ beam. The divergence of the exploring beam in the horizontal plane (plane of diffraction) was estimated to be ≪ 3 arc sec. Hence, specimen occupies the fourth crystal stage in symmetrical Bragg geometry for diffraction in (+, -, -, +) configuration. The specimen can be rotated about a vertical axis, which is perpendicular to the plane of diffraction, with minimum angular interval of 0.4 arc sec. The diffracted intensity is measured by using an in-house (National Physical Laboratory) developed scintillation counter. To provide two-theta (2θB) angular rotation to the detector (scintillation counter) corresponding to the Bragg diffraction angle (θB), it is coupled to the radial arm of the goniometer of the specimen stage. The rocking or diffraction curves were recorded by changing the glancing angle (angle between the incident X-ray beam and the surface of the specimen) around the Bragg diffraction peak position θB (taken as zero for the sake of convenience) starting from a suitable arbitrary glancing angle. The detector was kept at the same angular position 2θB with wide opening for its slit, the so-called ω scan.

The well-collimated and monochromated MoKα₁ beam obtained from the three monochromator Si crystals set in dispersive (+,-,-) configuration was used as the exploring X-ray beam. The MMTWD specimen crystal was aligned in the (+,-,-,+) configuration. The specimen can be rotated about the vertical axis, which is perpendicular to the plane of diffraction, with minimum angular interval of 0.4 arc sec. The diffraction curve (DC) was recorded by the so-called ω scan wherein the detector was kept at the same angular position 2θB with wide opening for its slit.
Before recording the diffraction curve, to remove the non-crystallized solute atoms remained on the surface of the crystal and also to ensure the surface planarity, the specimen was first lapped and chemically etched in a non preferential etchant of water and acetone mixture in 1:2 volume ratio. Figure 2.6 shows the high-resolution diffraction curve recorded for MMTWD single crystal specimen using MoKα₁ radiation in symmetrical Bragg geometry of the multicrystal X-ray diffractometer. The diffracting plane chosen to record the DC is (001). As seen in the figure, the DC contains only a single peak without any satellite peaks, which may be attributed to no internal structural grain boundaries present in MMTWD (Bhagavannarayanan et al 2005). The full width at half maximum (FWHM) of the diffraction curves is 124 arc s, which is higher than expected for a nearly perfect single crystal. The broadness of the curve shows that the crystal contains both vacancy and interstitial defects (Bhagavannarayana et al 2008 and Lal Bhagavannarayana et al 1989).

![Diffraction Curve](image_url)

**Figure 2.6** HRXRD curve of as-grown MMTWD single crystal recorded for (001) diffracting plane
2.4 LINEAR AND NONLINEAR OPTICAL STUDIES

Optical transparency is one of the important parameters to be optimized for the fabrication of NLO devices. The optical transmission spectrum of MMTWD crystal (thickness 1mm) was recorded using SCHIMADZU model UV-VIS spectrophotometer in the range 200 nm to 1100 nm. As-grown crystals of MMTWD showed 94% of transparency in the entire visible region as shown in Figure 2.7. UV cut-off wavelength for MMTWD is 360 nm. The cut-off wavelength of MMTC has been reported to be 373 nm. Compared to MMTC, 13 nm violet shift was observed in MMTWD. From the UV-VIS spectroscopy, it is observed that there is no absorption in the entire visible region and hence the material may be effective for second order nonlinear optical applications.

Figure 2.7 UV-Visible transmission spectrum of MMTWD single crystal
The linear refractive index of the MMTWD single crystal was measured using Abbey’s refractometer having the prism of refractive index 1.74. The measurement was performed on a single crystal of dimension 10\(\times\)5\(\times\)7 mm\(^3\). The crystal was polished with fine alumina powder. The source of monochromatic sodium vapor lamp of wave length 5893 Å was allowed to fall on the polished surface of the MMTWD single crystal. By adjusting the telescope, the critical angle of the outcoming beam was measured. The refractive index of the MMTWD was found to be 1.54 from the critical angle equation.

The SHG efficiency of the grown crystal was estimated by Kurtz and Perry (1968) technique. The fundamental beam of Q-switched Nd:YAG laser of wavelength 1064 nm was used to measure the SHG signal of MMTWD single crystal. The incident beam with pulse energy of 2.1 mJ/pulse and pulse width of 8 ns and repetition rate of 10Hz was employed. The fundamental beam was filtered using IR filter. The photomultiplier tube (Hamamatsu R2059) was used as a detector. From the output power measurement, the SHG efficiency of the MMTWD was found to be four times that of diaquatetrakis (thiocyanato) manganese (II) mercury (II)-N-methyl-2-pyrrolidone (MMTWMP).

2.5 FTIR AND LASER RAMAN STUDIES

The powdered crystal of MMTWD was subjected to FTIR studies to confirm the presence of functional groups and coordination of ligands. The spectrum was recorded in the range 400–4000 cm\(^{-1}\) as shown in the Figure 2.8. The main absorption peaks of MMTC, H\(_2\)O and DMA were observed in MMTWD. Appearance of bands in the high frequency region of 3379 cm\(^{-1}\), 3255 cm\(^{-1}\), 2953 cm\(^{-1}\), 2920 cm\(^{-1}\) correspond to the symmetric and asymmetric stretching of O-H and C-H groups respectively. The peak appeared at
2143 cm\(^{-1}\) corresponds to the C-N stretching frequency of the MMTWD. The C-S and C=O stretching mode are observed at 1593 cm\(^{-1}\) and 748 cm\(^{-1}\) respectively. The bands appeared at 482 cm\(^{-1}\) and 966 cm\(^{-1}\) show the presence of C-S bending and NCS overtone modes. Absorption peaks assigned for the O–H stretching modes of MMTWD appear at lower frequencies compared with pure water molecule due to the coordination of O atoms with the Mn atom. The hydrogen bonding is formed between H\(_2\)O and DMA molecules, in which H\(_2\)O act as a hydrogen bond donor and DMA act as hydrogen-bond acceptor, which cause weaker bonds between O and H in the coordinated H\(_2\)O molecule. The C–N and C–S stretching modes of MMTWD appear at shifted frequencies compared to MMTC, and the C=O stretching mode of MMTWD is shifted to a lower frequency compared to the corresponding frequency of the DMA. FTIR assignments of MMTWD, MMTC, H\(_2\)O and DMA molecules are compared in the Table 2.3.

![FTIR spectrum of MMTWD](image)

**Figure 2.8 FTIR spectrum of MMTWD**
Table 2.3 Comparison of FTIR assignments of MMTWD with MMTC, H₂O and DMA molecules

<table>
<thead>
<tr>
<th>Assignment</th>
<th>Frequency (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>MMTWD</td>
</tr>
<tr>
<td>υ (C-N)</td>
<td>2143</td>
</tr>
<tr>
<td>υ (C-S)</td>
<td>748</td>
</tr>
<tr>
<td>δ(NCS)</td>
<td>482</td>
</tr>
<tr>
<td>2δ (NCS)</td>
<td>966</td>
</tr>
<tr>
<td>υ (O-H)</td>
<td>3379</td>
</tr>
<tr>
<td>δ (O-H)</td>
<td>1421</td>
</tr>
<tr>
<td>υ (C-H)</td>
<td>2949</td>
</tr>
<tr>
<td>υ (C=O)</td>
<td>1593</td>
</tr>
<tr>
<td>δ (C-H)</td>
<td>1398, 1261</td>
</tr>
<tr>
<td>υ’ (C-N)</td>
<td>1018, 1197</td>
</tr>
</tbody>
</table>

Powdered sample of MMTWD was subjected to Laser Raman spectral analysis in the range 400 cm⁻¹ to 3000 cm⁻¹ and the corresponding spectrum is shown in Figure 2.9. The Raman peaks at 2130 cm⁻¹, 2139 cm⁻¹ and 2147 cm⁻¹ are assigned to C-N symmetric and asymmetric stretching vibration modes respectively. In a free thiocyanate (SCN⁻) ion of KSCN, the C-N stretching vibration appears at 2068 cm⁻¹ comparatively lower than that of coordinated SCN⁻ ion confirming the coordination of thiocyanate in MMTWD.
Figure 2.9 Laser Raman spectrum of MMTWD single crystal
The region around 400-600 cm\(^{-1}\) shows the NCS bending vibrational frequency. This coordination can be explained on the basis of electron transfer model. In MMTWD complex, metal ions of Mn\(^{2+}\) and Hg\(^{2+}\) act as electron acceptors and the ligands of thiocyanate (SCN\(^-\)) ion and dimethyl acetamide act as electron donors. Thus, an electron transforming from SCN\(^-\) ion to Hg\(^{2+}\) and Mn\(^{2+}\) ions significantly increases the C-N stretching vibration. The comparison of laser Raman vibrational frequencies of MMTWD with MMTC, DMA are given in Table 2.4. The results of laser Raman spectral analysis are complement to IR spectral analysis. The FTIR and Raman spectra of MMTWD single crystal agree well with the reported data (Wang et al 2003b).

Table 2.4 Comparison of laser Raman peaks of MMTWD with MMTC, H\(_2\)O and DMA molecules

<table>
<thead>
<tr>
<th>Assignment</th>
<th>Frequency (cm(^{-1}))</th>
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<tbody>
<tr>
<td></td>
<td>MMTWD</td>
</tr>
<tr>
<td>(\nu) (C-N)</td>
<td>2130, 2139, 2147</td>
</tr>
<tr>
<td>(\nu) (C-S)</td>
<td>748</td>
</tr>
<tr>
<td>(\delta) (NCS)</td>
<td>445, 463, 485</td>
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<tr>
<td>2(\delta) (NCS)</td>
<td>891, 925, 964</td>
</tr>
<tr>
<td>(\delta) (O-H)</td>
<td>1419</td>
</tr>
<tr>
<td>(\nu) (C-H)</td>
<td>2920</td>
</tr>
<tr>
<td>(\nu) (C=O)</td>
<td>1632</td>
</tr>
<tr>
<td>(\nu') (C-N)</td>
<td>1025, 1194</td>
</tr>
</tbody>
</table>
2.6 THERMAL ANALYSIS OF MMTWD COMPOUND

Thermal stability and physiochemical changes of MMTWD were studied by TGA, DTA analysis using NETZSCH Geratebau GmbH thermal analyser. Thermo gravimetric analysis and Differential thermal analysis of MMTWD sample were carried out from room temperature to 1000°C in the Nitrogen atmosphere at a heating rate of 20°C/min. The TGA and DTA curves for MMTWD are shown in Figure 2.10.

![Figure 2.10 TGA, DTA curves of MMTWD compound](image)

Thermal studies reveal that MMTWD is thermally stable upto 90°C, after this the sample undergoes weight loss appreciably. The change in weight loss confirms the decomposition of the sample. The percentages of weight loss from 90 °C to 110 °C and from 110 °C to 240 °C are 5.09 % and 24.62 %, respectively. This is very close to the theoretical weight loss of two-coordinated water molecule (5.16%) and two DMA (24.92%) in the
MMTWD compound. After 240 °C, breaking of three-dimensional network of remaining MMTC takes place, which leads to the liberation of HgS, MnS, carbon disulfide, cyanogen and nitrogen gases. The color of the pyrolysis product appeared as gray, with the weight percentage of 12.56%, which is close to the theoretical value of MnS (12.45%). From the DTA curve, appearance of two endothermic peaks indicates the loss of two coordinated water molecules and dimethyl acetamide molecule which agree well with the TGA measurements.

2.7 DIELECTRIC STUDIES

The dielectric studies on the (001) plane of MMTWD single crystal were performed using a HIOCKI 3532-50 LCR HITESTER instrument. The capacitance (C) and dissipation factor (D) of the MMTWD sample were measured as a function of frequency. The dielectric constant (ɛ’) and dielectric loss (ɛ’’ ) were calculated by the following relations

\[ ɛ' = \frac{C}{\varepsilon_o A} \]  \hspace{1cm} (2.3)  

and \[ ɛ'' = ɛ' D \]  \hspace{1cm} (2.4)

where \( \varepsilon_o \) is the permittivity of free space, \( t \) is the thickness of the sample and \( A \) is the area of cross section of the sample.

A polished sample of MMTWD with dimension 4 × 3.5 × 2 mm\(^3\) having graphite coating on opposite faces was placed between the two copper electrodes, which act as a parallel plate capacitor. The capacitance of the sample was measured by varying the frequency from 100 Hz to 5 MHz. Figure 2.11a shows the plot of dielectric constant (ɛ) versus applied frequency. The dielectric constant has higher value in the lower-frequency region (1kHz) and then decreases with the applied frequency upto 5 MHz. The dielectric constant has a higher value in the lower-frequency region
(5 Hz) and then decreases with the applied frequency upto 5 MHz, which is similar to that of MMTC (Joseph et al. 2006). Low value of dielectric constant is a suitable parameter for the enhancement of SHG coefficient (Miller 1964).

Figure 2.11 Variation of (a) dielectric constant and (b) dielectric loss with temperature and frequency
It is also observed that at lower frequencies and higher
temperatures, the dielectric constant is larger. Such variations observed at
higher temperature may be attributed to the blocking of charge carriers at the
electrodes. Because of the impedance to their motion at the electrodes, space
charge and macroscopic distortion results, which might cause larger values of
dielectric constant at lower frequencies (Arora et al 2004). Crystals with high
dielectric constant lead to power dissipation (Dalton 2003). The material
having low dielectric constant will have less number of dipoles per unit
volume. As a result, it may have minimum loss compared to the material
having high dielectric constant. MMTWD crystal possesses very low
dielectric loss at low frequencies (Figure 2.11b), which is attributed to good
quality of the crystal with less defects. Therefore MMTWD may be a
potential material for high-speed electro-optic modulations because of its low
dielectric constant.

2.8   LASER DAMAGE THRESHOLD MEASUREMENT

The utility of NLO crystal depends not only on the linear and
nonlinear optical properties but also largely on its ability to withstand high
power lasers (Boiling et al 1973 and Glass and Guenther 1973). Laser damage
threshold (LDT) is an important material parameter, the knowledge of which
is essential for using the crystal as an NLO element in various applications
involving large laser input power like frequency doubling, optical parametric
processes, etc. The damage threshold depends on many factors like pulse
duration, focal spot geometry, sample quality, experimental technique
employed, etc (Vanishri et al 2007). The one-on-one test uses only one single
shot on each unexposed site of the test samples, whereas the multiple shot test
was performed with multiple shot in the same location of the sample.
The selected surface of the MMTWD single crystals was polished with fine 4000 µ polishing sheet in order to have uniform surface quality. The single shot surface laser damage threshold of MMTWD was determined using Q-switched Nd-YAG laser of wavelength 1064 nm with a pulse width of 20 ns and 10 Hz repetition rate. The surface of the sample was placed at the focus of a lens of focal length 150 mm, focused beam diameter 237 µm and beam divergence 0.5 milliradians. The sample was mounted on movable translator which facilitates bringing in different regions of the sample for exposure precisely. The schematic of experimental setup used for laser damage threshold measurement is shown in Figure 2.12.

![Schematic of experimental setup used for laser damage threshold measurement](image)

**Figure 2.12** Schematic of experimental setup used for laser damage threshold measurement

While determining the single shot damage threshold, care was taken to select a fresh region after each shot, in order to avoid the cumulative effects resulting from multiple exposures. The onset of damage can be determined by means of visual spark and sound methods. The single shot surface laser damage threshold was determined to be 4.9 GW/cm². The laser damage threshold value obtained for MMTWD is moderately good for device point of view.
2.9 ETCHING STUDIES

Etching of surfaces using desirable solvent gives more information about the surface features. Patterns observed on surfaces like spirals, hillocks, and slip pattern, etc yield considerable information on the growth process and growth mechanism of the crystal. Etching studies on (001) plane of the MMTWD single crystal was carried out using water-DMA as an etchant. Optical microscopy was employed to study the surface features of the as-grown crystal. Good quality crystal with well defined morphology was carefully harvested from a mixed solvent of water and DMA (1:1) and gently dried with tissue and immediately transferred to optical microscopy. For the etching time of 5s and 10s, rectangular type etch pit patterns were observed as shown in Figure 2.13. The etchpit density of MMTWD compound was estimated to be $10^2$/cm$^2$ which shows good quality of the crystal for the fabrication of optical devices (Moitra and Kar 2007). The formations of rectangular etch patterns indicate the two-dimensional nucleation mechanism (Sangwal 1987).

![Figure 2.13 Etchpit pattern obtained for MMTWD single crystal](image-url)
2.10 CONCLUSION

Diaqua (Thiocyanato) Manganese Mercury–N,N-dimethylacetamide (MMTWD) material was synthesized by two step reaction process. The purity of the synthesized compound was confirmed by CHN elemental analysis. The solubility studies have been carried out using water-dimethyl acetamide mixed solvent. MMTWD single crystals were grown by slow cooling and slow evaporation methods. The tetragonal crystal structure and morphology of the MMTWD single crystal were determined using single crystal X-ray diffraction analysis. The crystallinity of the MMTWD was confirmed by well defined peaks of powder X-ray diffraction studies. The broad HRXRD curve shows the full width at half maximum (FWHM) of 124 arc s, which indicates the presence of vacancy and interstitial type point defects and the presence of single peaks without any additional peaks confirms the absence of low angle grain boundary in the MMTWD crystal. The coordination of water molecule and dimethyl acetamide was confirmed through FTIR and Raman spectroscopy studies. The grown crystal shows 94 % transmission with UV cut-off at 360 nm. The UV cut-off wavelength of this complex is lower than that of MMTC. The SHG efficiency of the MMTWD was measured to be higher than that of MMTWMP. The surface laser damage threshold is 4.9 GW/cm² and the value obtained for MMTWD seems to be moderately good from device point of view. The linear refractive index of the crystal was found to be 1.54. Thermal studies shows that the material is thermally stable up to 90° C. The increase in dielectric constant at low frequency is attributed to the space charge polarization. The etching studies reveal the formation of rectangular etch patterns, indicative of two dimensional (2D) growth mechanism.