CHAPTER 3

GROWTH AND CHARACTERIZATION OF
2-METHYLIMIDAZOLIUM d-TARTRATE
SINGLE CRYSTAL

3.1 INTRODUCTION

The requirement of noncentrosymmetry for SHG has been successfully designed in several organic systems using a number of strategies. The most obvious is the use of a single enantiomer of a chiral component which then guarantees crystallization into an acentric space group (Aakeroy et al 1992). In organic enantiomeric guest-host system, the guest molecule is an aromatic imidazolium cation that can be tailored through ring substitution and hydrogen-bonding ability to enhance the NLO responses. The host lattice is constructed with an enantiomeric monohydrogen tartrate anion that fulfils the noncentrosymmetric requirement and provides a constant contribution to the SHG efficiency. On the basis of this property, the growth of 2-Methylimidazolium d-Tartrate single crystal is grown by slow evaporation solution growth technique and SHG behavior of grown crystal was studied. 2-Methylimidazolium d-Tartrate was analyzed by single crystal X-ray diffraction. Fourier transform infrared spectroscopy, microhardness and dielectric studies were carried out. The theoretical factor group, UV-Vis-NIR spectral and Thermogravimetric / Differential thermal analyses were performed.
3.2 SYNTHESIS AND GROWTH OF 2-METHYLIMIDAZOLIUM d-TARTRATE

The 2-Methylimidazolium d-tartrate (C₈N₂O₆H₁₂) was synthesized and grown using mixed solvents of ethanol and deionised water. The equimolar (1:1) ratio of 2-Methylimidazole (C₄N₂H₆) and d (-) tartaric acid (C₄H₆O₆) were dissolved separately in ethanol and deionised water, respectively. The solutions of individually prepared raw materials were mixed together. The mixture of solutions was found to be turbid, so ethanol and deionised water were added and stirred well for four hours by using a motorized magnetic stirrer till a clear solution was obtained. The solution was filtered using Whatman (grade no.1) filter paper in clean vessels and vessels containing the solution were closed with perforated polythene covers and housed in the constant temperature bath at 33°C. Nucleation was observed (speck formation) in a week and the crystal was allowed to grow for two weeks. The reaction is shown in the Figure 3.1. The crystal of size 10 mm × 5 mm × 3 mm is obtained as shown in Figure 3.2.

\[
\begin{align*}
\text{C₄N₂H₆} & \quad + \quad \text{C₄H₆O₆} \quad \rightarrow \quad \text{C₈N₂O₆H₁₂} \\
\text{2-Methylimidazole} & \quad \text{d(-) tartaric acid} \quad \text{2-Methylimidazolium d-tartrate}
\end{align*}
\]

Figure 3.1 Reaction scheme of 2-Methylimidazolium d-tartrate
3.3 CHARACTERIZATION OF 2-METHYLIMIDAZOLIUM d-TARTRATE CRYSTALS

3.3.1 X-ray Diffraction Studies

The grown crystals of 2-Methylimidazolium d-tartrate were confirmed by single crystal X-ray diffraction analyses.

3.3.1.1 Single crystal XRD analysis

The single crystal X-ray diffractometer (Model Nonius CAD-4/MACH) with MoKα (0.71073Å) radiation was used to obtain the accurate cell parameters of the grown 2-Methylimidazolium d-tartrate crystals at room temperature by the least-square refinement of the setting angles of 25 reflections. The obtained lattice parameters are presented in Table 3.1, which are in good agreement with the reported values (Fuller et al 1995). It is confirmed from the single crystal XRD data that the grown crystal belongs to monoclinic crystal system with noncentrosymmetric space group P2₁.
Table 3.1 Crystallographic data of 2-Methylimidazolium d-tartrate

<table>
<thead>
<tr>
<th>Lattice parameters</th>
<th>Present Work</th>
<th>Reported Value (Fuller et al 1995)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>4.725 (2) Å</td>
<td>4.739 (1) Å</td>
</tr>
<tr>
<td>b</td>
<td>16.258 (4) Å</td>
<td>16.281 (3) Å</td>
</tr>
<tr>
<td>c</td>
<td>6.716 (4) Å</td>
<td>6.746 (1) Å</td>
</tr>
<tr>
<td>α</td>
<td>90º</td>
<td>90º</td>
</tr>
<tr>
<td>β</td>
<td>100.89º (4)</td>
<td>100.895º (3)</td>
</tr>
<tr>
<td>γ</td>
<td>90º</td>
<td>90º</td>
</tr>
<tr>
<td>V</td>
<td>506.6 (4) Å³</td>
<td>511.12 (16) Å³</td>
</tr>
</tbody>
</table>

3.3.2 Spectral Analysis

3.3.2.1 Factor group analysis of 2MImdT crystal

The factor group and the site group are important in the application of group theoretical methods. An additional advantage of the factor group method is that it provides a basis for the prediction of the infrared and Raman spectra of lattice vibrations.

2MImdT (C₈N₂O₆H₁₂) crystallizes in the monoclinic crystal system with the noncentrosymmetric space group P₂₁(C₂). The procedure outlined by Rousseau et al (1981) and Tell et al (1966) was followed to carry out the factor group analysis of the title compound. The factor group analysis of 2MImdT is carried out using the character table for the point group C₁(2). The unit cell consists of two molecules. A single molecule of 2MImdT contains 28 atoms which in turn gives rise to 168 modes. Group theoretical analysis of the fundamental modes of 2MImdT crystal reveal that there are 168 vibrational optical modes and are seen to decompose into $\Gamma_{\text{total}} = 82A + 83B$ among
which three acoustic modes $\Gamma_{\text{acou}} = A + 2B$ are excluded, that corresponds to block transition of the crystal. The results are presented in Table 3.2.

**Table 3.2  Results of Factor group analysis of 2-Methylimidazolium d-tartrate crystal**

<table>
<thead>
<tr>
<th>Factor group symmetry</th>
<th>A</th>
<th>B</th>
</tr>
</thead>
<tbody>
<tr>
<td>(C(^2))</td>
<td></td>
<td></td>
</tr>
<tr>
<td>External modes</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(i) Translational</td>
<td>1</td>
<td>2</td>
</tr>
<tr>
<td>(ii) Rotational</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>Internal modes</td>
<td>78</td>
<td>78</td>
</tr>
<tr>
<td><strong>Total</strong></td>
<td>82</td>
<td>83</td>
</tr>
</tbody>
</table>

Polarizability tensors associated with monoclinic crystals like 2MImdT are of the form

$$A = \begin{pmatrix} \alpha_{xx} & \alpha_{xy} & 0 \\ 0 & \alpha_{yy} & 0 \\ 0 & 0 & \alpha_{zz} \end{pmatrix}, \quad B = \begin{pmatrix} 0 & 0 & \alpha_{xz} \\ 0 & 0 & \alpha_{yz} \\ 0 & 0 & 0 \end{pmatrix}$$

The polarizability tensors are depicted along the crystallographic X,Y and Z axes. Phonons belonging to A and B are both Raman and infrared active. The summary of the factor group analysis of 2MImdT is presented in Table 3.3.
Table 3.3 Factor group analysis – summary

<table>
<thead>
<tr>
<th>Factor group symmetry ( (C_2^2) )</th>
<th>Site symmetry ( C_1 (2) )</th>
<th>( C )</th>
<th>( N )</th>
<th>( O )</th>
<th>( H )</th>
<th>Optical Mode</th>
<th>Acoustic Mode</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>External mode</td>
<td>Internal mode</td>
<td>( T )</td>
<td>( 3R )</td>
<td>78</td>
<td>24</td>
<td>6</td>
<td>18</td>
<td>36</td>
</tr>
<tr>
<td>B</td>
<td>( 2 )</td>
<td>( T )</td>
<td>( 3R )</td>
<td>78</td>
<td>24</td>
<td>6</td>
<td>18</td>
<td>36</td>
</tr>
<tr>
<td>Total</td>
<td>( 3 )</td>
<td>( T )</td>
<td>( 6R )</td>
<td>156</td>
<td>48</td>
<td>12</td>
<td>36</td>
<td>72</td>
</tr>
</tbody>
</table>

3.3.2.1.1 Vibrational analysis of 2MImdT

Analysis on the vibrational spectra reveals information regarding the nature of bonding, structures of co-ordination compounds and material confirmation.

The molecular structure of 2MImdT enumerates that the title compound consists of O–H, N–H and C–H groups etc. The calculated vibrations of 2MImdT could be due to lattice vibrations and internal vibrations of these groups. The formal classification of fundamental mode reveals 156 internal vibrations which can be attributed as 78A + 78B and external modes contributed by 3 translational (A + 2B) and 6 rotational (3A + 3B) modes.

The bands observed between 4000 cm\(^{-1}\) and 500 cm\(^{-1}\) in Figure 3.3 arise from the internal modes of 2MImdT. The bands obtained below 450 cm\(^{-1}\) arise from the deformational vibrations and the liberation and translational modes of anions and cations. Table 3.4 presents the correlation scheme obtained by following the procedures of Fateley et al (1972). Each
internal mode of 2-Methylimidazolium d-tartrate ions splits into two components of \( A(Z) \), \( B(X) \) and \( B(Y) \) are IR active and \( A(\alpha_{xx}, \alpha_{yy}, \alpha_{zz}, \alpha_{xy}) \) and \( B(\alpha_{xz}, \alpha_{yz}) \) are Raman active.

**Table 3.4 Correlation scheme of 2MImdT**

<table>
<thead>
<tr>
<th>Site symmetry</th>
<th>Factor group symmetry</th>
<th>Activity</th>
</tr>
</thead>
<tbody>
<tr>
<td>( C_1(2) )</td>
<td>( C_2^2 )</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Raman</td>
</tr>
<tr>
<td>( A^{168} )</td>
<td>82A</td>
<td>( \alpha_{xx}, \alpha_{yy}, \alpha_{zz}, \alpha_{xy} )</td>
</tr>
<tr>
<td></td>
<td>83B</td>
<td>( \alpha_{xz}, \alpha_{yz} )</td>
</tr>
</tbody>
</table>

**3.3.2.1.2 Internal vibrations**

As the 2-MImdT molecules do not have any symmetry the internal vibrations exhibited are of both infrared and Raman active exclusive of acoustic mode. The internal vibrations of 2-MImdT may be classified as those arising from O-H, C-H and N-H functional groups. These vibrations are strongly coupled between themselves.
3.3.2.1.3 External vibrations

The bands observed below 500 cm\(^{-1}\) are mainly due to external modes, the rotational and translational modes of the ions. The rotational modes are expected to have higher frequency and intensity than translational modes in Raman spectra. However, the translational modes are more intense in FT-IR spectra (Bhattacharjee 1990, Hanuja and Fomitsev 1980). In the present investigation 2-MImdT is expected to have 9 modes in Raman at low frequency range corresponding to external modes. They are distributed as (A+3R) translational and (2A+3R) rotational modes. These vibrations can be achieved experimentally by polarized Raman measurements.

3.3.3 Fourier Transform Infrared Spectroscopy

The mid-Fourier Transform Infrared spectrum of 2-Methylimidazolium d-tartrate was recorded at room temperature in the region 4000 cm\(^{-1}\) – 400 cm\(^{-1}\) by JESCO 416 PLUS FT-IR Spectrometer equipped with LiTaO\(_3\) detector, KBr beam splitter and He-Ne Laser source boxcar apodization used for 250 averaged interfergram collections for both the sample and background using KBr pellet technique. The recorded FT-IR spectrum of the title compound is shown in Figure 3.3 and functional group assignments were made using the standards (Barbara Hachula et al 2010). A strong and broad band, extending over the frequency range 3400 cm\(^{-1}\) – 1700 cm\(^{-1}\) with the maximum at 2713 cm\(^{-1}\), indicates the presence of a hydrogen bond. The absorption band at 3100 cm\(^{-1}\) arises from the stretching vibrations of the C-H bonds of methyl group. The N-H stretches of imidazole ring produce broad intense signals between 2000 cm\(^{-1}\) and 3000 cm\(^{-1}\). In the present case a very strong peak occurs at 2968 cm\(^{-1}\), which indicates the functional groups of the imidazole ring. The band at 1582 cm\(^{-1}\) is attributed to the C=O stretch of carbonyl group. The peak at 1217 cm\(^{-1}\) is due to
C-H bending vibration of aromatic ring. The peak at 1072 cm\(^{-1}\) is due to the C-O stretching.

![FTIR Spectrum of 2-MIImdT](image)

**Figure 3.3 FTIR Spectrum of 2-MIImdT**

### 3.4 OPTICAL STUDIES OF 2-MIImdT CRYSTAL

It is well known that the parameters such as optical transmittance range and lower cutoff wavelength are important to tailor the materials for specific applications. The transmittance spectrum of 2-Methylimidazolium d-tartrate is recorded in the range 200 nm–800 nm using CARY 5E UV-Vis-NIR Spectrophotometer and the recorded spectrum is shown in Figure 3.4. From the spectrum it is observed the title compound has low absorption in the entire visible region. The absence of the substantial absorption in the entire visible region might enable the achievement of microscopic NLO response
with non zero values. This low absorption behavior is an added advantages of nonlinear optical materials and the lower cutoff wavelength is found at 290 nm. This absorption leads to promotion of pairs of nonbonding electrons from nitrogen and oxygen for interactions with $\pi$ electrons of the ring. This characteristic behavior is attractive to frequency conversion applications since these compounds do not absorb radiation in the visible region of the electronic spectrum.

Figure 3.4 UV-Vis spectrum of 2-MImdT crystal

The dependence of optical absorption coefficient with the photon energy helps to study the band structure and type of transition of electrons (Tigau et al 2004). The optical absorption coefficient ($\alpha$) was calculated from the transmittance using the following relation

$$ \alpha = \frac{2.3036 \log \left( \frac{1}{T} \right)}{d} $$

(3.1)
where $T$ is the transmittance and $d$ is the thickness of the crystal. In the high photon energy region, the energy dependence of absorption coefficient suggests the type of band gap. As an indirect band gap semiconductor, the crystal under study has an absorption coefficient ($\alpha$) obeying the following relation for high photon energies ($h\nu$):

$$(\alpha h\nu)^{1/2} = A (E_g - h\nu)$$

where, $E_g$ is the optical band gap of the crystal, and $A$ is a constant. The variations of $(\alpha h\nu)^{1/2}$ versus $h\nu$ in the fundamental absorption region are plotted in Figure 3.5 and $E_g$ can be evaluated by extrapolation of the linear part (Amit Kumar Chawla et al 2006). The optical band gap is found to be 4.5 eV.

![Figure 3.5](image-url)  
**Figure 3.5** The dependence of $(\alpha h\nu)^{1/2}$ on the photon energy $h\nu$
3.4.1 Determination of Optical Constants

The refractive index can be determined from the reflectance (R) data using (Kaid and Ashour 2007)

\[ R = \frac{(n-1)^2}{(n+1)^2} \]  

(3.3)

and the transmittance (T) is given by

\[ T = \frac{(1-R)^3 \exp(-\alpha t)}{1-R^2 \exp(-2\alpha t)} \]  

(3.4)

The reflectance in terms of the absorption coefficient can be derived from the above equations. Hence,

\[ R = \frac{1 \pm \sqrt{1-\exp(-\alpha t) + \exp(\alpha t)}}{1+ \exp(-\alpha t)} \]  

(3.5)

and from the above data the refractive index \( n \) can also be derived as

\[ n = \frac{-(R+1) \pm \sqrt{-3R^2 + 10R - 3}}{2(R-1)} \]  

(3.6)

Figure 3.6 shows that the refractive index \( n \) decreases with increasing wavelength of the incident light beam, owing to interactions of photons and electrons.
3.5 DIELECTRIC STUDIES OF 2-MImdT CRYSTAL

The dielectric measurement in crystal gives the information about distribution of electric field within the crystalline solid (Vijayan et al 2008). Studies of the temperature and frequency dependence of dielectric properties can unveil useful information about structural changes, defect behavior, and transport phenomena (Marder et al. 1991). The dielectric constant and the dielectric loss of 2-Methylimidazolium d-tartrate sample were measured using a HIOKI 3532-50 LCR HITESTER in the frequency region 50 Hz to 5 MHz. Figure 3.7 shows the variations of dielectric constant with frequency. The dielectric constant of the sample was calculated for varying frequencies under different temperatures from 35ºC to 75ºC. It is observed from the Figure 3.7 that the dielectric constant decreases exponentially with increase in frequency and then attains almost a constant value in the high frequency region. At room temperature, dielectric constant decreases with increase in frequency.
It is observed that as the temperature increases, the value of dielectric constant increases as shown in Figure 3.8. At lower frequency and at higher the temperature there is a larger dielectric constant. Such variations at high temperature may be attributed to blocking of charge carriers at the electrodes. The impedance variations at the electrodes cause space charge and macroscopic distortion, resulting in larger values of dielectric constant at lower frequencies. With increasing temperature, a high degree of dispersion in the permittivity begins to occur at lower frequency. This could be again due to thermally generated charge carriers from the onset of space charge to electric field conduction. The characteristic of low dielectric constant with high frequency in the title compound suggests that the sample possesses enhanced optical quality with lesser defects and this parameter is important for various nonlinear optical applications.

Figure 3.7 Variation of dielectric constant of 2-MImdT crystal with frequency
Figure 3.8 Variation of dielectric constant of 2-MImdT crystal with temperature

The change in dielectric loss (tan δ) with frequency is shown in Figure 3.9. It is observed that the dielectric loss decreases with increase in frequency. The low value of dielectric loss indicates good quality (Benet and Gnanam 1994). The low dielectric loss with high frequency supports the enhanced optical quality with lesser defects and this property is of vital importance for NLO applications (Varma et al 1983) of the crystal. The larger value of dielectric constant and dielectric loss at lower frequencies may be attributed to space charge polarization owing to charged lattice defects (Smyth 1965).
The conductivity of 2-Methylimidazolium d-tartrate increases with increase in temperature as shown in Figure 3.10. The electrical conduction in dielectrics is mainly a defect controlled process in the low temperature region.
3.6 TGA-DTA ANALYSIS OF 2MImdT

The thermogravimetric analysis (TGA) was carried out on the 2-Methylimidazolium d-tartrate crystals. TGA spectrum was recorded in Nitrogen atmosphere between room temperature and 700°C using SDT Q600 V8-3 Build 101 Unit. The recorded TGA spectrum of 2-Methylimidazolium d-tartrate is shown in Figure 3.11. There is no weight loss up to 188°C. There is no inclusion of water in crystal lattice, which was used as the solvent for crystallization. The thermogram spectrum reveals that the major weight loss (99.15%) starts at 188.25°C and continues up to 226.90°C. The nature of weight loss indicates the decomposition point of the material. However below this temperature no weight loss is observed. In DTA spectrum an endothermic peak observed at 196.84°C corresponds to the decomposition temperature of the 2-Methylimidazolium d-tartrate.
3.7 SHG CONVERSION EFFICIENCY OF 2-MImdT

The nonlinear conversion efficiency measurement has been made using the Kurtz and Perry powder technique (1968). A Q-switched Nd:YAG laser beam of wavelength 1064 nm with input beam energy 2.7mJ/pulse and pulse width 8 ns with repetition rate of 10 Hz was used. The grown crystal of 2-Methylimidazolium d-tartrate is powdered and packed in a micro capillary of uniform bore and exposed to laser radiation. A green flash emission from the title sample was observed which indicates the NLO behavior of the material.

3.8 HARDNESS

The structure and composition of the crystalline solids were inviolably related to the mechanical hardness. Hardness of a material is the
measure of resistance it offers to local deformation. In case of crystals, it can be understood in terms of resistance offered to dislocation motion. In general, it comes from the intrinsic resistance of crystals and the resistance caused by imperfection in the crystal (Kotry et al 1989). The Hardness measurements were made on the prominent (100) plane of 2MImdT at room temperature using Leitz Wetzier tester with Vicker’s pyramidal diamond indenter. Loads ranging from 5 g to 40 g were used for making indentations, keeping the time of indentation constant at 3 sec for all the cases. The diagonal lengths of the indentation mark and crack length were measured, using the micrometer eyepiece at a magnification of 200X. The Vicker’s hardness value was estimated from the in equation (2.2)

A plot between the hardness number and the load is depicted in Figure 3.12(a). As the load increases, the hardness value increases. It exhibits the reverse indentation size effect. A plot shown in 3.12 (b) obtained between log (P) and log (d) gives more or less a straight line. The relation connecting the applied load and diagonal length d of the indentor is given by Meyer’s law

\[ P = ad^n \]  \hspace{1cm} (3.7)

Here, n is the Meyer’s index or work hardening coefficient that has been calculated from the slope of the straight line. The value of n obtained for 2MImdT is 1.0. From careful observations on various materials Onitsch (1947) pointed out that n lies between 1 and 1.6 for moderately hard materials and more than 1.6 for soft materials. This confirms that the grown crystal is hard. From the hardness value, the yield strength \( \sigma_y \) can be calculated (Cahoon et al 1971). For \( n < 2 \), the applicable formula is \( \sigma_y = H_v/3 \). It is seen from Figure 3.12 (c) that yield strength also increases with increase in load.
Figure 3.12 (a) Plot between load and hardness number for 2-MImdT crystal

Figure 3.12 (b) Plot between log P and log d for 2-MImdT crystal
3.9 CONCLUSION

Bulk single crystals of 2-Methylimidazolium d-tartrate were grown by slow evaporation solution growth method. The optical studies show the absence of absorption above 290 nm. The SHG efficiency is comparable to that of the standard KDP crystal. From FT-IR spectrum, the presence of intermolecular hydrogen bonding is observed, which could enhance the nonlinear property of the material. The occurrence of $\pi - \pi^*$ transitions in the carboxyl group accounts for the nonlinearity in the title compound. The normal dielectric behavior is observed in 2MImdT crystal. The harness study reveals that the crystal is moderately hard. Group theoretical analysis of the 2-Methylimidazolium d-tartrate reveals that there are 168 optical modes, which are seen to decompose into $\Gamma_{\text{total}} = 82A + 83B$ apart from three acoustic modes (A+2B). The thermogram of 2-Methylimidazolium d-tartrate reveals the incipient melting occurs at 196.84°C. It can be concluded that the 2MImdT crystal suitability in the NLO applications.