CHAPTER 3

STUDIES ON GROWTH AND CHARACTERIZATION OF 2-METHYLIMIDAZOLIUM HYDROGEN SUCCINATE

3.1 INTRODUCTION

There is a need of the development of new organic species with enhanced structural, optical, thermal, dielectric, mechanical and nonlinear optical properties (NLO). Engineering the NLO properties for efficient second harmonic generation (SHG) efficiencies need to have several physical and structural requirements which are to be monitored (Chemla and Zyss 1987). The growth of nonlinear optical materials has received a great deal of attention in developing commercial applications in the fields of optical communication, signal processing, sensing and instrumentation. The requirement of noncentrosymmetry for SHG has been successfully designed into several organic systems using a number of strategies (Fuller et al. 1995). Salts of dicarboxylic acids are organic compounds held together by short acid bridges (Samantha K. Callear et al. 2010). In the packing of molecules they are held together by six intermolecular hydrogen bonds and crystallizes in the noncentrosymmetric space group (Barbara Hachula et al. 2009 and Barbara Hachula et al. 2011).

The term imidazole implies a five membered, heterocyclic ring system containing tertiary nitrogen and imino group. The names oxazole and thiazole designate five membered ring systems containing in addition to tertiary nitrogen, an oxygen or sulphur atom
(Xiang-Gao Meng et al. 2009 and Ławniczak et al. 2009). The design of organic crystals for NLO applications is supported by the molecules containing π electrons which are highly polarizable. An organic molecule having high first order hyperpolarizability exhibits good nonlinear optical properties. Hence the search for new materials possessing NLO properties has been a thirst for developing changes in many fields. 2-methylimidazole, a compound widely used as a chemical intermediate in the manufacture of pharmaceuticals, photographic and photothermographic chemicals, dyes, pigments, agricultural chemicals and rubber (Anshu Srivastava 2011).

The asymmetric unit contains hydrogen succinate anion and 2-methylimidazolium cation. The various physical and chemical properties of imidazole complexes with dicarboxylic acid salts were reported in the literature (Gunes Suheyla Kurkuoglu et al. 2011 and Fatih Semerci et al. 2010). The heterocyclic molecules are joined together by N-H---O bond with the acid molecules. The nitrogen containing heterocyclic compounds known to crystallize by a hydrogen bond network, where the protons can easily migrate (Fred B. Stocker et al. 2000). The unit contains the succinate anion lying in the mirror plane with 2-methylimidazole moieties crystallizes in noncentrosymmetric space group Cmc21, which is favourable for second harmonic generation. The molecules are packed with six intermolecular hydrogen bonds into three dimensional networks (Xiang-Gao Meng et al. 2009 and Srinivasan et al. 2011).

In this present investigation the growth, structural, spectral, thermal, mechanical, dielectric and second harmonic generation of 2-methylimidazolium hydrogen succinate are carried out and discussed in a lucid manner.
3.2 SYNTHESIS, SOLUBILITY AND GROWTH

1:2 molar quantities of succinic acid and 2-methylimidazole were dissolved separately using double distilled water in a 25 ml beaker and stirred for 10 minutes in a constant temperature bath at 32°C. Then the separately prepared solutions were mixed together in a 100 ml beaker. The solution was optimally closed and housed in the constant temperature bath at 40°C for slow evaporation. The synthesized product of the title compound was collected after 10 days and the product was systematically confirmed by powder XRD and FT-IR analysis before growth. Before starting crystal growth, solubility in deionized water was estimated at different temperatures and the solubility diagram is shown in Figure 3.1.

![Figure 3.1 Solubility curve of 2-methylimidazolium hydrogen succinate](image)

The reaction scheme is shown in Figure 3.2 (a). The saturated solution of 2MISA was prepared at an ambient temperature and the solution was transferred in a 100 ml beaker and stirred continuously for 2 hours. The prepared homogeneous solution was filtered with Whatman No. 1 filter sheets
in a clean 100 ml beaker for crystallization. The beaker containing the solution was optimally closed and housed in the constant temperature bath with an accuracy of ± 0.01°C. The solution was continuously monitored and the growth solution turned to pale yellowish in color. Nucleation was observed in 14 days. After a period of 25 days platelet colorless single crystal of appreciable size was harvested as shown in Figure 3.2 (b).

**Figure 3.2 (a) Reaction scheme of 2-methylimidazolium hydrogen succinate**

**Figure 3.2 (b) As grown single crystal of 2-methylimidazolium hydrogen succinate**
3.3 CHARACTERIZATION

The grown single crystal was subjected to single crystal X-ray diffraction as well as powder X-ray diffraction analyses. From the X-ray diffraction studies, it is confirmed that the grown crystal belongs to the orthorhombic crystal system. The structural perfection was studied using HRXRD. The functional groups of the synthesized compound were confirmed by FT-IR and Raman spectral studies. The UV-Visible, Photoluminescence, Thermal analyses (TG/DTA) were carried out to study the optical and thermal stability of the grown crystal. The mechanical and dielectric properties were analysed.

3.3.1 Single Crystal X-ray Diffraction Analysis

The single crystal X-ray diffraction data were collected using a monochromated MoKα (λ = 0.7107Å) radiation. The single crystal of dimension 0.1 × 0.1 × 0.1 mm³ was cut and mounted on a glass fiber using cyanoacrylate. The unit cell parameters were determined by collecting the diffracted intensities from 36 frames measured in three different crystallographic zones at room temperature. The crystallographic data obtained for 2MISA are presented in Table 3.1. It is observed that the grown crystal belongs to the orthorhombic system with space group Cmc2₁.

Table 3.1 Single crystal XRD data of 2MISA

<table>
<thead>
<tr>
<th>Lattice parameters</th>
<th>Observed values (Å)</th>
<th>(Xiang-Gao Meng et al 2009) (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a</td>
<td>6.75 (5)</td>
<td>6.801 (10)</td>
</tr>
<tr>
<td>b</td>
<td>8.10 (2)</td>
<td>8.158 (11)</td>
</tr>
<tr>
<td>c</td>
<td>17.34 (10)</td>
<td>17.438 (2)</td>
</tr>
</tbody>
</table>
3.3.2 Powder X-ray Diffraction Analysis

Powder X-ray diffraction pattern was recorded using BRUKER D2 Phaser, powder X-ray diffractometer with CuKα radiation (λ = 1.5418 Å). The powdered sample of 2MISA was scanned in steps of 0.2° over a 2θ range of 10-70° and the recorded X-ray diffraction pattern is shown in Figure 3.3. The prominent peaks were assigned using powderX software package. From the X-ray diffraction pattern it is observed that the highest intensity corresponds to (004) plane. It is confirmed that the grown crystal belongs to the orthorhombic crystal system.

![Powder X-ray diffraction pattern of 2MISA](image)

**Figure 3.3** Powder X-ray diffraction pattern of 2MISA

3.3.3 Structural Perfection Analysis - High Resolution X-ray Diffraction

To evaluate the crystalline perfection, the rocking curve (Figure 3.4) was recorded for a typical single crystal specimen using (110)
diffracting planes in symmetrical Bragg geometry (as discussed in section 1.11.1.2) by employing the multicrystal X-ray diffractometer with MoK$_{\alpha 1}$ radiation. The solid line (convoluted curve) is well fitted with the experimental points represented by the filled circles. On deconvolution of the diffraction curve, it is clear that the curve contains two humps, which are attached to the central peak. The main peak corresponds to the internal structural low angle boundary whose FWHM is 105 arc sec from their adjoining regions. On deconvolution of the diffraction curve, it is clear that the curve contains two additional peaks, which are 90 and 86 arc sec away from the central peak. These two additional peaks from their adjoining regions correspond to two internal structural very low angle boundaries. The full width at half maximum (FWHM) of the boundaries are 52 and 132 arc sec as depicted in the Figure 3.4.

Though the crystal contains a low angle boundary, the low angular spread of around 700 arc sec of the diffraction curve (DC) indicates that the quality of the crystal is fairly good. It may be mentioned here that such a low angle boundary could be detected with well-resolved peak in the diffraction curve only because of the high-resolution of the multicrystal X-ray diffractometer used in the present studies. The influence of such defects may not cause much effect on the NLO properties. Impurities of raw materials can greatly influence the growth of crystal. It is interesting to see the asymmetry of the DC. For a particular angular deviation ($\Delta \theta$) of glancing angle with respect to the peak position, the scattered intensity is much more in the positive direction in comparison to that of the negative direction. This feature clearly indicates that the crystal contains predominantly interstitial type of defects than that of vacancy defects (Lal and Bhagavannarayana 1989).
Figure 3.4 HRXRD pattern recorded for (110) diffracting plane for a typical 2MISA crystal by employing a Multicrystal X-ray diffractometer

Hence the lattice undergoes compressive stress thereby decreasing the d spacing, increases the scattered intensity slightly more than that of Bragg angle. The effect of such a low angle boundary may not be very significant in device applications. Thermal fluctuations or any mechanical disturbances during the growth period may cause this change.

3.3.4 Vibrational Studies

Vibrational studies were carried out using FT-IR and Raman measurements in the range 4000-400 cm$^{-1}$. The recorded spectra are shown in Figures 3.5 and 3.6. The vibrational assignments reveal the presence of functional groups that are present in the synthesized compound.
3.3.4.1 FT-IR spectrum

The FT-IR spectrum of the grown crystal was recorded in the range 4000 to 400 cm\(^{-1}\) as mentioned in section (1.11.2.1) in the first chapter. The recorded spectrum is shown in Figure 3.5. The N-H stretching vibration of imidazolium moiety occurs at 3121 cm\(^{-1}\). The CH\(_2\) stretching vibrations of succinic acid molecule are seen at 2943 cm\(^{-1}\). The C=O vibration of succinate gives peaks at 1694 and 1640 cm\(^{-1}\). The peak at 1573 cm\(^{-1}\) is assigned to ring vibration of imidazolium moiety. The CH\(_2\) bending modes appear at 1425 and 1330 cm\(^{-1}\). The C-N vibrations appear at 1183 and 1063 cm\(^{-1}\) (Silverstein et al 1981). The imidazolium C-H bending mode gives a group of peaks below 1000 cm\(^{-1}\). As there is no peak close to 3410 cm\(^{-1}\) the succinic acid might be in the complete ionized state. A sharp peak at 1962 cm\(^{-1}\) is due to a combination band derived from the peaks at 1063 and 887 cm\(^{-1}\).

![Figure 3.5 FT-IR spectrum of 2-methylimidazolium hydrogen succinate](image-url)
3.3.4.2 Raman spectroscopy

Raman spectroscopy deals the measurement of wavelength and intensity of inelastically scattered light from molecules or crystal lattices. Excitation line at 632.8 nm was provided by air cooled He-Ne laser. Figure 3.6 shows the Raman spectrum of 2MISA. The peak at 1512 cm\(^{-1}\) was more intense than others. As this vibration would have more change in polarizability than others, they appear intense. The peaks appear at 2180 cm\(^{-1}\), 3165 cm\(^{-1}\) are due to N-H vibrations. The CH\(_2\) stretching vibration gives its peak at 2929 cm\(^{-1}\). The imidazolium moiety gives rise to an intense peak.

![Raman spectrum of 2-methylimidazolium hydrogen succinate](image)

**Figure 3.6** Raman spectrum of 2-methylimidazolium hydrogen succinate

3.3.5 Factor Group Analysis

C\(_4\)H\(_7\)N\(_2\)^+.C\(_4\)H\(_5\)O\(_4\)^- crystallizes in orthorhombic crystal system with space group Cmc\(_2\)_1 with four molecules per unit cell. Factor group method is applicable to review the vibration behavior of crystals from their symmetry
properties. 2MISA belongs to the orthorhombic crystal system, crystallizes in a space group Cmc2\(_1\) with site symmetry \(C^6_{2v}\). Also it provides a basis for the prediction of theoretical IR and Raman spectra of the lattice. A single molecule contains 26 atoms which gives rise to \((26 \times 4)\) 104 atoms in the unit cell. Group theoretical analysis of the fundamental modes of 2MISA predicts that there are 156 vibrational modes. Thus 144 internal modes and 9 external modes such as 3 Translational, 6 Rotational and 3 acoustical modes. The total possible irreducible modes of vibrations can be divided into four factor group species which decompose into \(\Gamma_{153} = 38 A_1 + 39 A_2 + 38 B_1 + 38 B_2\) and three acoustic modes (\(A_1 + B_1 + B_2\)). The factor group analysis was performed by following the procedure outlined by Rousseau et al. (1981) and the summary is presented in Table 3.2. Here the polarizability tensors are depicted along the crystallographic X, Y and Z axes. Phonons belonging to \(A_2(Z), B_1(Y)\) and \(B_2(X)\) are Infrared active and \(A_1 (\alpha_{xx}, \alpha_{yy}, \alpha_{zz}), A_2 (\alpha_{xy}), B_1 (\alpha_{xz}), B_2 (\alpha_{yz})\) are Raman active (Fateley et al. 1972). In orthorhombic crystals like 2MISA the associated polarizability tensors are of the form

\[
A_1 = \begin{pmatrix}
\alpha_{xx} & 0 & 0 \\
0 & \alpha_{yy} & 0 \\
0 & 0 & \alpha_{zz}
\end{pmatrix}
\quad A_2 = \begin{pmatrix}
0 & \alpha_{xy} & 0 \\
0 & 0 & \alpha_{xz} \\
0 & 0 & 0
\end{pmatrix}
\quad B_1 = \begin{pmatrix}
0 & 0 & \alpha_{xy} \\
0 & 0 & 0 \\
0 & 0 & 0
\end{pmatrix}
\quad B_2 = \begin{pmatrix}
0 & 0 & \alpha_{yz} \\
0 & 0 & 0 \\
0 & 0 & 0
\end{pmatrix}
\]

<table>
<thead>
<tr>
<th>Factor group symmetry</th>
<th>(C_1) Site symmetry</th>
<th>Ext</th>
<th>Int</th>
<th>C</th>
<th>H</th>
<th>N</th>
<th>O</th>
<th>Optical modes</th>
<th>Acoustical modes</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>(A_1)</td>
<td>T, 2R 36</td>
<td>12</td>
<td>18</td>
<td>3</td>
<td>6</td>
<td>39</td>
<td>1</td>
<td>38</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(A_2)</td>
<td>- 36</td>
<td>12</td>
<td>18</td>
<td>3</td>
<td>6</td>
<td>39</td>
<td>-</td>
<td>39</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(B_1)</td>
<td>T, 2R 36</td>
<td>12</td>
<td>18</td>
<td>3</td>
<td>6</td>
<td>39</td>
<td>1</td>
<td>38</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(B_2)</td>
<td>T, 2R 36</td>
<td>12</td>
<td>18</td>
<td>3</td>
<td>6</td>
<td>39</td>
<td>1</td>
<td>38</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>3T, 6R 144</td>
<td>48</td>
<td>72</td>
<td>12</td>
<td>24</td>
<td>156</td>
<td>3</td>
<td>153</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Vibrational studies give a signature of the nature of chemical bonding among materials. From the spectral analysis it is confirmed that the O-H groups are protonated and counter balance the negative charge of the nitrogen ion functionality. Thus, the molecular structure of the synthesized compound was confirmed by the spectral analysis. The C-O and NH\textsubscript{2} group frequencies in the molecules are held together by a network of hydrogen bonds. The internal vibrations of 2MISA may be classified into those arising from functional groups NH\textsubscript{2}, C-H and C-O. However, their vibrations may be strongly coupled between themselves. The correlation scheme is given in Table 3.3.

**Table 3.3 Correlation scheme of 2MISA**

<table>
<thead>
<tr>
<th>Factor group symmetry</th>
<th>IR Active</th>
<th>Raman Active</th>
</tr>
</thead>
<tbody>
<tr>
<td>38A\textsubscript{1}</td>
<td>-</td>
<td>(a_{xx}, a_{yy}, a_{zz})</td>
</tr>
<tr>
<td>39A\textsubscript{2}</td>
<td>Z</td>
<td>(a_{xy})</td>
</tr>
<tr>
<td>38B\textsubscript{1}</td>
<td>Y</td>
<td>(a_{xz})</td>
</tr>
<tr>
<td>38B\textsubscript{2}</td>
<td>X</td>
<td>(a_{yz})</td>
</tr>
</tbody>
</table>

**3.3.6 TG/DTA**

Thermogravimetric and differential thermal analyses as mentioned in section 1.11.3 give information regarding the thermal stability of the grown crystal. Figure 3.7 (a, b) shows the TG/DTA traces recorded for the compound 2MISA with a heating rate of 20°C/min in the temperature range up to 500°C in N\textsubscript{2} atmosphere. From the TGA trace (Figure 3.7 (a)) the absence of solvent entrapment during the crystallization process is noted. It is confirmed by the absence of weight loss at TGA trace. TGA infers that there
is a single stage weight loss, owing to the liberation of volatile substances with the result of gradual weight loss of around 4% at 498.6°C. There is no inclusion of water in the crystal lattice which was used for growing single crystals. The endothermic peak at 176°C in the DTA trace (Figure 3.7 (b)) shows the melting point. The sharpness of thermogram is an illustrative of crystalline purity. From this it is identified that there is no phase transition up to its melting point and this enables the suitability of the crystal for NLO applications. There is a small hump at around 250°C in DTA trace owing to the decomposition of the compound.

![Figure 3.7 TG/DTA trace of 2-methylimidazolium hydrogen succinate](image)

**Figure 3.7** TG/DTA trace of 2-methylimidazolium hydrogen succinate

### 3.3.7 Optical Studies

The optical studies were performed for the grown molecular crystal in the UV-Vis-NIR region (200-1400 nm) using Perkin Elmer unit and the recorded absorbance spectrum is shown in the Figure 3.8 (a). A good optical transmittance of about 85-89% as shown in Figure 3.8 (b), is the necessary
condition for a desirable NLO applications. The UV-Vis-NIR spectrum gives information about the structure of the molecule because the absorption of UV and visible light involves the promotion of electron in s and p orbitals from the ground state to higher energy states. The transition occurs between $\pi-\pi^*$ or it may be $\sigma-\sigma^*$. When absorption is monitored from low wavelength to high wavelength region the lower cutoff occurs at 330 nm, which is due to the presence of 2-methylimidazole and succinic acid moieties. They show a very little absorption in the UV region which can be attributed to the presence of the reacting species (Ren et al 2000).

Figure 3.8 (c) shows the relation between the product of absorption coefficient and the incident photon energy $(\alpha h\nu)^{1/2}$ with the photon energy $h\nu$ at room temperature. The optical bandgap $(E_g)$ is estimated using Equation (2.1). The optical bandgap of the crystal is found to be 3.8 eV. The value of optical bandgap shows its suitability for photonic and optoelectronic applications. The refractive index can be determined from the reflectance (R) data using the Equation (2.5) as mentioned Chapter 2.

The absorption coefficient $(\alpha)$ is given by McLean's formula (Marinova and Veleva 2002), where $t$ is the thickness of the sample

$$T = \frac{(1-R)^2 \exp(-\alpha t)}{1-R^2 \exp(-2\alpha t)} \quad (3.1)$$

The reflectance in terms of absorption coefficient can be derived from the above Equation 3.1. Figures 3.8 (c) and 3.8 (d) show the obtained optical bandgap and the variation of refractive index with energy respectively. By tailoring the optical parameters the suitability of materials for device fabrications can be obtained.
Photoluminescence (PL) spectrum of 2MISA crystal was recorded using the excitation wavelength 400 nm and the spectrum is shown in Figure 3.9. The spectrum shows a broad peak centered at 530 nm with intensity comparable to that of other organic compounds. Intensity gradually decreases in the higher wavelength region. The maximum intensity peak gives rise to green emission. The lowering of photoluminescence intensity at higher wavelength region may be attributed to a relatively low barrier for rotation of
the carboxyl group around the central C-C bond. The addition of imidazolium moiety may reduce multiple emissions.

![Photoluminescence spectrum of 2MISA crystal](image)

**Figure 3.9 Photoluminescence spectrum of 2MISA crystal**

### 3.3.9 Mechanical Studies

Microhardness indentations have been extensively applied at the microstructural level (Arivuoli et al 1991). The mechanical stability is extremely important as far as the fabrication of devices is concerned. Hardness of a material is a measure of the resistance it offers to local deformation. 2MISA single crystals with (110) plane was tested for their microhardness properties using a Vicker’s indentation tester. The measurements were made at room temperature and the indentation time was kept at 5 sec. The hardness of the crystal is calculated using the relation as mentioned in Equation (1.7).
The microhardness value was taken as the average of the several impressions made. The variation of hardness with indenter load for the grown single crystal is shown in Figure 3.10 (a), which gives that the hardness value increases on increasing the load. Indentation size varies depending upon the surface of the indented sample. The relation between P and d is given by Meyer’s relation using Equation 2.2. Frictional and elastic effects lead to the normal indentation size effect (ISE), while indentation cracking contributes to the reverse ISE. The reverse ISE can be caused by (a) the relative predominance of nucleation and multiplication of dislocations and (b) the relative predominance of the activity of either two sets of slip planes of a particular slip system or two slip systems below and above a particular load. The value of n determines the work hardening coefficient.

Figure 3.10  Variation of (a) hardness behaviour of 2MISA (b) log P vs log d (c) Stiffness constant with load (d) Yield strength with respect to applied load
For the normal ISE behaviour, the exponent \( n < 2 \). When \( n > 2 \), there is reverse ISE behaviour. When \( n = 2 \), the hardness is independent of the applied test load and is given by Kick’s law (Sangwal et al 2006). ISE is caused by the generation of cracks around indentation. At a particular load the surface chipping swamps the process of generation of cracks and the indentation size no longer increases with the increase of load. From the linear fit the value of Meyer’s index ‘n’ is 2.3 (Figure 3.10 (b)). When the applied load increases, crack occurs due to the elastic stress formed beneath the indenter and the smooth surface of the crystal surface during indentation. As a result fracture preceded by a crack, which is due to the neighboring planes gains the energy during the impact. The stiffness constant gives an idea about the nature of bonding between neighboring atoms. This is the property of the material by virtue of which it can absorb maximum energy before fracture occurs (Wooster 1953). For various loads the stiffness constant is calculated using Wooster’s empirical Equation (2.4).

The variation of elastic stiffness constant with load is shown in Figure 3.10 (c). From the hardness value \( H_v \), the yield strength of the material can be found using the Equation (2.3). Figure 3.10 (d) shows the plot of load dependent yield strength (Bamzai et al 1998).

### 3.3.10 Dielectric Measurements

The dielectric analysis is an important tool used to know the details about the electrical properties of material at different frequencies. The sample was specially mounted on a three terminal device holder as mentioned in section 1.11.6. The dielectric permittivity and dielectric loss were measured for different frequencies at room temperature (Figure 3.11 (a, b)). The dielectric permittivity \( \varepsilon_r \), is due to polarization of materials and four primary
mechanisms of polarization include electronic $\alpha_e$, ionic $\alpha_i$, orientational $\alpha_o$ and space charge polarizations.

**Figure 3.11** Variation of (a) dielectric permittivity (b) dielectric loss (c) a.c conductivity with respect to log frequency

The space charge polarization occurs when mobile charge carriers favour charge migration. The charges get piled up resulting into a localized polarization in the material. At very low frequencies the dielectric characteristics are influenced by interfacial polarization or at the microscopic level by space charge polarization (Moulson and Herbert 1990). Thus the high value of dielectric permittivity at low frequency is mainly due to the space
charge polarization. The dielectric permittivity ($\varepsilon_r$) was computed using the relation (2.6) as mentioned in the second chapter.

The variation of dielectric permittivity occurs when log freq. is 2-2.8, which favours the displacement of charge carriers more at room temperature. When log freq. $> 2.8$ change of dielectric permittivity is independent of frequency. The dielectric loss also decreases monotonically with increase in frequency (Badr et al 2011 and Firdous et al 2010). The variation of dielectric loss is similar to that of dielectric permittivity. Using the values of dielectric permittivity ($\varepsilon_r$) and dielectric loss ($\tan \delta$), the values of conductivity $\sigma_{ac}$ can be calculated using the Equation (2.5) as mentioned in chapter 2.

The $\sigma_{ac}$ is independent of frequency up to 10 kHz and above this frequency it increases according to the power law

$$\sigma_{ac} \propto \omega^n \quad (3.2)$$

The increase of conductivity with frequency is observed. The ac conductivity is found to be high at high frequency (Figure 3.11 (c)) owing to polaron hopping. The value of conductivity $\sigma_{ac}$, is comparable with those obtained for other ionic conductors (Baran et al 1999). The symmetric dielectric tensor can be expressed as below for an orthorhombic crystal system. The components are $\varepsilon_{xx}$, $\varepsilon_{yy}$ and $\varepsilon_{zz}$.

$$
\begin{pmatrix}
\varepsilon_{xx} & 0 & 0 \\
0 & \varepsilon_{yy} & 0 \\
0 & 0 & \varepsilon_{zz}
\end{pmatrix}
$$
The dielectric permittivity was measured experimentally along a, b and c axes. Dielectric tensor (three axes) for the grown single crystal was determined as a function of frequency at room temperature. The dielectric permittivity along a, b and c axes was measured (Figure 3.12).

**Figure 3.12** Dielectric permittivity (tensorial components) along the three axes a, b and c

The variation of dielectric permittivity values along the three axes is due to the variation of dielectric polarization which occurs when an electric field is applied (Fapeng Yu et al 2010). The dielectric values vary as 843-440 (a-axis), 685-192 (b-axis) and 578-112 (c-axis).

### 3.3.11 Nonlinear Optical Studies

Kurtz-Perry powder technique is the widely used technique for confirming SHG of materials (Kurtz and Perry 1968). The crystal was
powdered and packed densely. The fundamental laser beam of 1064 nm wavelength, 8 ns pulse with 10 Hz pulse rate was made to fall normally on the sample cell. The power of the output beam was measured using a power meter. The green light was detected by a photomultiplier tube and displayed on a storage oscilloscope. The powdered materials of KDP and urea crystals were identical in size and used as reference materials in the SHG measurement. The powder form of 2MISA exhibits a green light showing the presence of SHG property.

3.4 CONCLUSION

Single crystal of 2-methylimidazolium hydrogen succinate was grown by slow evaporation solution growth technique. The optical transparency is found to be quite good and so 2MISA is a potential material for NLO applications. The single crystal XRD confirmed that 2MISA crystallizes in orthorhombic crystal system with a space group of Cmc21. High Resolution X-ray diffraction study showed the crystalline perfection is reasonably good. Functional groups were assigned using FT-IR and Raman spectra. Factor group analysis predicts the active modes in IR and Raman. From the UV-Visible absorbance and transmittance the bandgap and refractive index were explored. PL spectrum shows the green emission. The dielectric permittivity and dielectric loss decrease with increasing frequency. The ac conductivity increases with increasing frequency. Thermal studies reveal the crystal is stable up to 176°C. Microhardness studies enumerate the variation of hardness number, stiffness constant and yield strength with the applied load. The SHG output of the material is confirmed by the emission of green signal. Based on these facts, it could be proposed that this novel material can be better accommodated for optical applications.