CHAPTER 7

Growth and characterization of an organic single crystal –

Dye doped Hippuric acid

7.1 Introduction

Nonlinear optical (NLO) materials have attracted and increasing attention due to their wide applications in the recent technologies like lasers, optical communication and data storage [1]. Second Harmonic Generation (SHG) measurements of organic nonlinear optical materials have already produced results, which by far, supersede those obtained from all the known inorganic alternatives. The polar organic materials from noncentro-symmetric crystal structure which gives rise to second-order nonlinear optical properties [2,3]. Organic nonlinear optical materials are often formed by week van der waals and hydrogen bonds and hence possess high degree of delocalization. Organic materials are molecular materials those after unique opportunities for fundamental research as well as for technological applications [4].

Search for a new NLO material with high optical nonlinearity, chemical flexibility, mechanical strength and thermal stability is very essential to fulfill the increasing demand in the field of telecommunication, optical computing and optical data storage. In the nucleation and growth of certain nonlinear optical crystals, amino acids play a vital role. Many natural amino acids individually exhibit the nonlinear optical properties [5] because they have a donor NH$_2^+$ and acceptor COO$^-$ and also intermolecular charge transfer is possible.

Hippuric acid (HA) namely N-benzoyl-glycine or benzoylaminoacetic acid, is a colorless crystal obtained from the urine of domestic animals and also in smaller amounts in human urine [6]. Also it is one of the organic nonlinear optical materials which exhibit a good Second Harmonic Generation (SHG). Liebig [7] is the first who discovered hippuric acid which was isolated from equine urine and in contrast to benzoic acid, it contains nitrogen. Hippuric acid (HA) with molecular formula [C$_6$H$_5$.CO.NH.CH2.COOH] is also referred to as benzamino acetic acid. Its structural formula is shown in Fig. 7.1 and the
molecular structure is shown in Fig. 7.2. It crystallizes in the orthorhombic space group P212121. The SHG behavior and NLO properties of HA crystal was studied by several workers [8–10]. Recently the influence of aniline on the growth and characterization of benzoyl glycine single crystals [11], benzophenone and iodine doped benzoyl glycine single crystals are reported [12]. The X-ray crystallographic structure of HA was determined by Ringertz [13]. Refat et al. [14] reported the Mn(II), Au(III) and Zr(III) complexes with HA that synthesized and characterized by elemental analysis, molar conductivity, magnetic measurements, spectral methods and simultaneous thermal analysis techniques. The DFT studies of Hippuric acid was reported by Karaback[15]. DFT studies have been made on the conformation and spectroscopic behaviors of the HA carried out with the combined Becke’s three-parameter exchange functional in combination with the Lee, Yang and Parr correlation functional (B3LYP) exchange-correlation energy functions.

![Fig.7.1 structural formula of Hippuric acid](image_url)
Rhodamine is a dye, an organic molecule well-studied in laser physics and nonlinear optics for its fluorescent properties. Solutions of this dye are commonly used in biology as a staining fluorescent dye for optical microscopy and in optical applications to provide laser gain media. Dyeing of crystals is a practice that was developed particularly for quantum optics applications, because of very significant increase in surface area achieved in growing crystals. Here the studies namely, the growth details, single crystal XRD, FTIR, TGA/DTA, NLO studies and optical transmission of DHA (Dye doped Hippuric acid) single crystals are reported in the present investigation.
7.2. Experimental

The commercially available Rhodamine B and Hippuric acid AnalR grade (Merck GR) was taken purified by repeated recrystallization process. The recrystallized salt was used for the present studies. To grow bulk crystals from solution using isothermal solvent evaporation technique, it is desirable to select a solvent in which it is moderately soluble. So, we have determined the solubility of HA in various solvents such as water, acetic acid, methanol, ethanol, ethyl acetate, acetone and dimethyl formamide. The solubility of hippuric acid crystals was greater in acetone than in other solvents. Hence acetone was selected as the solvent for the growth of doped hippuric acid crystals. The slow evaporation method was followed to obtain Rhodamine doped hippuric acid crystals and 0.01 M% of Rhodamine B was added to hippuric acid and dissolved in acetone. The solution was stirred continuously for 6 hours. The solution was filtered using ultra micro-pore filter paper. Then the saturated solution was allowed to cool at room temperature and kept in a vibration free area with a
tightly closed plastic cover. Good quality single crystals of Hippuric acid have been collected from the mother solution in a time span of 5 days. The photographs of the as grown crystals DHA are shown in Fig. 7.4.

![Fig. 7.4 Grown single crystal of DHA](image)

7.3 Characteristic studies

7.3.1 Single-crystal X-ray Diffraction

Single crystal X-ray diffraction analysis was carried out to determine the lattice parameters. The single crystal diffraction analysis of DHA (Dye doped Hippuric acid) was carried out using Bruker Kappa Apex II single crystal X-ray diffractometer with MoKα radiation (λ = 0.71069 Å). The lattice parameters obtained from this measurement are listed in Table 7.1. These values agreed well with the reported values the grown crystal and retain its original structure. This result reveals that, the Rhodamine B has entered into the lattice sites of Hippuric acid.
Table 7.1 XRD data and cell volume of Doped Hippuric crystals

<table>
<thead>
<tr>
<th>Crystal</th>
<th>a (Å)</th>
<th>b (Å)</th>
<th>c (Å)</th>
<th>Cell volume (Å³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure HA (JCPDS)</td>
<td>9.116</td>
<td>10.594</td>
<td>8.862</td>
<td>855.84679</td>
</tr>
<tr>
<td>Pure HA (reported) [8]</td>
<td>9.117</td>
<td>10.577</td>
<td>8.874</td>
<td>855.72433</td>
</tr>
<tr>
<td>(NaCl)HA</td>
<td>9.249616</td>
<td>10.81215</td>
<td>8.8024</td>
<td>880.312</td>
</tr>
<tr>
<td>(KCl) HA</td>
<td>8.96739</td>
<td>10.89748</td>
<td>8.84491</td>
<td>864.33706</td>
</tr>
<tr>
<td>Rhodamine doped HA</td>
<td>8.92</td>
<td>9.15</td>
<td>10.65</td>
<td>868.9</td>
</tr>
</tbody>
</table>

7.3.2 CHN analysis

The CHNS elemental analysis was carried out for the Rhodamine doped crystal by using Perkin-Elmer Series II 2400 CHNS/O Elemental Analyser. The result of elemental analysis shows the composition of the crystal is the following (in wt.%): C: 62.73 H: 3.87, N: 7.51 as shown in Table 2. After summing up these, the resultant value of 74.11 wt.% clearly confirms the addition of Dye material. The micro analysis of the grown crystalline material shows an agreement with the calculated values and confirmed the stiochiometric ratio.

Table 7.2 Percentage of CHN in pure and doped hippuric acid crystals

<table>
<thead>
<tr>
<th>Crystal</th>
<th>C%</th>
<th>H%</th>
<th>N%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure HA (JCPDS)</td>
<td>60.33</td>
<td>5.06</td>
<td>7.82</td>
</tr>
<tr>
<td>HA[16]</td>
<td>60.25</td>
<td>5.20</td>
<td>7.80</td>
</tr>
<tr>
<td>Rhodamine doped HA</td>
<td>62.73</td>
<td>3.87</td>
<td>7.51</td>
</tr>
</tbody>
</table>
7.3.3 Fourier Transform Infra-Red Spectroscopy

The mid Fourier transform infrared spectrum of Rhodamine B doped Hippuric acid was recorded at 300 K in the range of 4000–400 cm$^{-1}$ using the KBr pellet technique. The spectrum of DHA is shown in Fig. 7.5 and the recorded FTIR assignments are tabulated in Table 7.2. The frequencies with their relative intensities were obtained in FTIR of doped hippuric acid. Assignments were made on the basis of relative intensities, magnitudes of the frequencies and from the literature data. The peak observed at 3337 cm$^{-1}$, 1485 cm$^{-1}$ and 435 cm$^{-1}$ are mainly due to asymmetric stretching, bending and out of plane deformation of N-H group of vibrations. The band appears at 2936 cm$^{-1}$ is mainly due to C-H stretching mode of vibration. Similarly the band appears at 1306 cm$^{-1}$ and 723 cm$^{-1}$ are assigned to C-H in plane and out of plane deformations respectively. Among the major peaks the intense absorption at 1749 and 1616 cm$^{-1}$ is attributed to C=O asymmetric and symmetric stretching vibrations of COOH group. Aromatic ketones have absorption band due to the in-plane deformation vibration of C–CO group at 542 cm$^{-1}$. CH$_2$–CO deformation at 1416 cm$^{-1}$ supported the presence of methyl group. The effect of Rhodamine B on the functional groups of the pure Hippuric acid crystal has been identified by the FTIR spectrum at its positions as shown in the spectra, exactly matches with each other due to overlapping of bonds although there is a change in organic elements percentage due to the addition of dopants.

Table 7.3. FTIR Assignments of Doped Hippuric acid (DHA)

<table>
<thead>
<tr>
<th>S.no</th>
<th>Wavenumber -cm$^{-1}$</th>
<th>Band assignments</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3337</td>
<td>N-H Asymmetric stretching</td>
</tr>
<tr>
<td>2</td>
<td>2936</td>
<td>C-H symmetric stretching</td>
</tr>
<tr>
<td>3</td>
<td>1749</td>
<td>C=O Asymmetric stretching</td>
</tr>
<tr>
<td>4</td>
<td>1616</td>
<td>C=O symmetric stretching</td>
</tr>
<tr>
<td>5</td>
<td>1485</td>
<td>N-H bending</td>
</tr>
<tr>
<td>6</td>
<td>1416</td>
<td>CH$_2$-CO deformation</td>
</tr>
<tr>
<td>7</td>
<td>1306</td>
<td>C-H in plane deformation</td>
</tr>
<tr>
<td>8</td>
<td>723</td>
<td>C-H out of plane deformation</td>
</tr>
</tbody>
</table>
7.3.4 Optical Studies

An optical absorption spectrum of the pure and doped hippuric acid crystal was carried out between 200 and 1100 nm using LAMDA-35 UV-VIS-NIR spectrophotometer. Optical study is an important parameter for an NLO crystal. The optical studies of DHA crystals dissolved in distilled water were recorded in the UV-Vis. spectral region. In DHA the transmittance between 560 and 1100 nm is approximately 100%, is an advantage and is the key requirement for materials having NLO properties. It is observed that the lower cutoff of DHA crystal is reduced around 200 nm compared with pure one. The Hippuric acid crystal is well fitted with the reference values [16]. Absence of absorption in the region between
400 and 1200 nm, as shown in Fig. 7.6, is an advantage as it is the key requirement for materials having NLO properties.

**Fig. 7.6 UV-Visible Spectrum of pure and Doped Hippuric acid (DHA)**
7.3.5 SHG Efficiency Studies

The study of nonlinear optical conversion efficiency has been carried out using the modified experimental setup of Kurtz and Perry technique [17,18]. A Q-switched Nd: YAG laser beam of wavelength 1064 nm, pulse width of 8 ns and with a repetition rate of 10 Hz was used. The grown single crystal of DHA was powdered with a uniform particle size and then packed in a micro capillary of uniform bore and exposed to laser radiations. The output from the sample was monochromated to collect the intensity of 532 nm component. The generation of the second harmonics was confirmed by the emission of green light. The SHG conversion efficiency of DHA is found to be about 0.6 times that of KDP.

7.3.6 Thermo gravimetric analysis

Thermo analytical methods involve the measurement of various properties of materials subjected to dynamically changing environments under predetermined condition of heating rate, temperature range and gaseous atmosphere or vacuum. Among all the thermal methods, the most widely used techniques are TGA, DTA and DSC which find extensive use in all fields of inorganic and organic chemistry, metallurgy, mineralogy and many other areas.

In many cases, the use of a single thermo analytical technique may not provide sufficient information to solve the problem on hand and hence the use of other thermal techniques, either independently or simultaneously for complementary information becomes necessary. For example, both differential thermal analysis (DTA) and thermo gravimetric analysis (TGA) are widely used in studies involving physicochemical changes accompanied by variation in the heat content and the weight of the material.

The thermo gravimetric analysis deals with the change in the mass of a substance, continuously monitored as a function of temperature when it is heated. The Differential Thermal analysis (DTA) shows the variation of heat flow with temperature. The present investigation of doped Hippuric acid crystals have been studied by employing TGA/DTA in order to study the effect of doping on thermal stability of DHA crystals. The thermal stability of the grown crystals was studied by the thermo gravimetric analysis (TGA) and DTA using
Perkin Elmer Thermal Analysis Instrument and Netzsch Instrument. The TGA was carried out in nitrogen atmosphere at a heating rate of 5\(^0\) C/min in the temperature range of 50–800\(^0\)C.

The TGA curve area and DTA curves are shown in Fig.7.7. The thermogram of PHA crystal shows that the decomposition starts at 210\(^0\) C and afterwards a sharp decrease in weight is observed up to 275.5\(^0\) C [19]. Thermal decomposition of DHA crystal begins at 207\(^0\) C and ends at 314\(^0\) C. a slight increment is observed in first stage of decomposition temperature of doped crystals, suggesting that Rhodamine B has modified the thermal stability of PHA crystals. A sharp endotherm at about 194.3\(^0\) C for DHA is due to the melting of DHA crystals. The melting point and the thermal stability of the doped crystals were found to be varying from pure hippuric acid crystals [20]. The changes in the parameters are due to the incorporation of Rhodamine B atoms into the lattice and it clearly indicates that these materials are suitable for NLO applications. The sharpness of this peak shows the good degree of crystallinity of the sample. Thermo analytical data and percentage of decomposition of DHA crystals are listed in Table 7.4.

**Table 7.4 Thermo analytical data of DHA crystals**

<table>
<thead>
<tr>
<th>Crystal</th>
<th>Decomposition Temperature</th>
<th>DTA Peaks</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure HA (reported) [14]</td>
<td>210(^0)C --- 275.5(^0)C</td>
<td>189.1(^0)C</td>
</tr>
<tr>
<td>(NaCl)HA</td>
<td>213.13(^0)C --- 300(^0)C</td>
<td>186.9(^0)C</td>
</tr>
<tr>
<td>(KCl) HA</td>
<td>215(^0)C --- 312(^0)C</td>
<td>187.8(^0)C</td>
</tr>
<tr>
<td>Rhodamine doped HA</td>
<td>207(^0)C --- 314(^0)C</td>
<td>194.3(^0)C</td>
</tr>
</tbody>
</table>
7.3.7 Dielectric Studies

For NLO materials characterizations, dielectric study is one of the important parts. Because it does not only throw light on the materials behavior under the influence of applied electric field but also its applications.

In general, for any molecules will have two possibilities when influenced by an external field,

1. Molecules may have permanent dipole moments which may be aligned in an external field.
2. The distances between ions or atoms may be influenced by external field.

However, the polarization in atoms or molecules is induced by an external field by displacing electrons with respect to the corresponding nuclei.

Dielectric study of NLO material is very important because the operation of electro-optic devices is based on the Pockel’s effect in which the
change in the dielectric constant is a linear function of applied field [21]. Microelectronics industry requires replacement of dielectric materials in multilevel interconnect structures with new low dielectric constant materials as an interlayer dielectric (ILD), which surrounds and insulates interconnecting wirings. Lowering the dielectric constants of the ILD decreases the RC delay, lowers the power consumptions and reduces the “crosstalk” between the nearby interconnects [22]. Therefore, many attempts were made to study the reduction dielectric constant values of the doped systems.

In present study, the dielectric studies of the grown single crystal of DHA were carried out using HIOKI 3532 -50 LCR meter in the frequency range of 50 Hz and 5MHz at various temperatures. For the measurement of dielectric permittivity, dielectric loss and A.C conductivity of doped organic single crystal DHA prepared and mounted between two copper platforms and electrodes. The samples were cut and polished using wet cloth polishing sheet. The sample is electroded on either side with silver paste to make it to behave like parallel plate capacitor. The resistance, capacitance and dissipation factor values are directly measured for LCR meter.

Dielectric permittivity and loss

The dielectric constant and dielectric loss of the sample are calculated from capacitance and dissipation factor. The dielectric constant of the DHA crystal is calculated through the capacitance by the fundamental equation

\[
\varepsilon_r = \frac{Cd}{\varepsilon_o A}
\]

Where C is the capacitance, d is thickness of the sample, \(\varepsilon_o = 8.854 \times 10^{-12} Fm^{-1}\) is the permittivity of free space and A is the area of cross section.

The variation of dielectric constant as a function of frequency of doped crystal DHA are shown in Fig. 7.8. The contribution of the electric, ionic, orientation and space charge polarizations which depend on the frequencies of dielectric constant observed from the diagram and indicating that the grown crystals possesses improved pyroelectric properties [23,24]. At low frequencies, all the four contributions are active. The very low value of
dielectric constant at higher frequencies is important for the enhancement of SHG coefficient.

The variation of dielectric loss as a function of frequency of doped crystal DHA are shown in Fig. 7.9. The dielectric loss (\(\tan\delta\)) is calculated by the equation

\[
\tan \delta = \varepsilon_r D
\]

Where, D is the dissipation factor. A material must have low dissipation factor for device fabrication. It is observed that the dielectric loss decreases with increasing frequency. The larger values of dielectric loss at lower frequencies may be attributed to space charge polarization owing to charged lattice defects [25]. The very low dielectric loss reveals the very high purity of the crystals [26]. These curves suggest that dielectric loss is also strongly dependent on the frequency of the applied field.

![Graph showing dielectric constant vs Log f](image)
7.3.8. AC Conductivity studies

The Fig.7.10. shows variation of ac conductivity for different frequencies. From the diagram, it is observed that the frequency increases the a.c resistivity decreases.

The AC conductivity is calculated using the relation

\[ \sigma_{ac} = \omega \varepsilon_0 \varepsilon_r \tan \delta \]

where, \( \omega \) is angular frequency of applied electric field. The AC conductivity of the DHA crystals feebly increases up to the logarithmic of 6.30 HZ. From the sharp increase observed in the logarithmic frequency at 6.47 Hz indicates the dielectric breakdown frequency of the material.
7.3.9. Vicker’s microhardness measurement

One of the best methods to determine the mechanical stability of the materials is the microhardness testing. The hardness of the grown crystals of DHA were made using Leitz-Wetzlar hardness tester fitted with a Vickers diamond pyramidal indenter. The transparent polished crystal free from cracks was selected for hardness measurements. The transparent crystal was mounted on the platform of the microhardness tester and variations of loads (25-100g) were applied. The indentation time was fixed as 10 ns.

The Vicker’s hardness was calculated using the standard formula

\[ H_v = \frac{1.8544P}{d^2} \quad \text{Kg/mm}^2 \]
Where $H_v$ is the Vickers hardness number in Kg/mm$^2$, $P$ is the applied load in Kg, $d$ is the diagonal length in mm.

A graph plotted between hardness number ($H_v$) and applied load ($P$) as shown in Fig.7.11. From the graph it was observed that Vickers hardness number ($H_v$) increases with in increases load.

Elastic stiffness and yield strength measurement

The microhardness value correlates with other mechanical properties namely yield strength ($\sigma_y$) and elastic stiffness constant ($C11$). Yield strength is a point at which material exceeds the elastic limit and will not return to its origin shape or length if the stress is removed. Yield strength is one of the important properties for device fabrication which can be calculated by the relation,

$$\sigma_y = \frac{H_v}{3}$$

The elastic stiffness constant gives an idea about tightness of bonding between neighbor atoms and it was calculated using Wooster’s empirical relation as [27-30]

$$C11 = \frac{H_v^{7/4}}{d}$$

The elastic stiffness constant and yield strength are tabulated in Table.7.5

<table>
<thead>
<tr>
<th>Load (P) g</th>
<th>$H_v$ (kg/mm$^2$)</th>
<th>$C_{11}$ ($\times 10^{-3}$ M Pa)</th>
<th>$\sigma_y$ (M Pa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>47</td>
<td>8.274</td>
<td>153.643</td>
</tr>
<tr>
<td>50</td>
<td>56.4</td>
<td>11.384</td>
<td>184.371</td>
</tr>
<tr>
<td>100</td>
<td>64.5</td>
<td>14.40</td>
<td>210.85</td>
</tr>
</tbody>
</table>

Meyer index ($n$)

The materials are classified by the Meyer’s index number. The Meyer’s index number is calculated from the Mayer’s law, which relates the load and indentation diagonal length.

$$P = kd^n$$

Where $k$ is the material constant and $n$ is the Mayer’s index (or work-hardening coefficient). The above relation indicates that $H_v$ should increase with the increase in $P$ if $n > 2$ and
decrease with $P$ when $n < 2$. The ‘$n$’ value is determined from the plot of $\log P$ vs. $\log d$, as shown in Fig.7.12. The slope of the plot of $\log P$ versus $\log d$ gives the work hardening index ($n$) and that is found to be 2.599. The value of the work hardening index($n$) number of the grown crystal DHA is greater than 2. The material is confirmed as hard material with amount of mechanical strength which is better for device fabrications [31].

**Fig. 7.11.** Load vs Hardness

**Fig. 7.12** LogP vs Log d
7.4. Conclusion

The single crystals of doped hippuric acid were grown by solution growth method for the first time with good quality. Its lattice dimensions were calculated from the single crystal XRD analysis. The FT-IR study portrays the presence of different functional groups in the crystals. Its optical behavior was assessed by UV–Vis. Spectroscopy. TGA and DTA studies reveal that the presence of dopants changes the thermal stability of the crystals. It is observed that DHA has 0.6 times relative SHG efficiency than that of KDP. The dielectric studies of the doped crystals give the details of dielectric constant and dielectric loss. The low values of dielectric constant and dielectric loss are suitable for NLO devices. The mechanical stability of the Doped crystals studied by Vickers microhardness test. The mechanical studies reveal that the doped crystals are hard material. Thus the good NLO properties, excellent optical quality and moderate thermal stability makes the doped hippuric acid crystals, a strong candidate for NLO applications.
Reference


