EFFECT OF MALEIC ACID ON THE GROWTH AND CHARACTERIZATION STUDIES OF HIPPURIC ACID NLO SINGLE CRYSTAL

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Abstract. Good quality single crystals of pure hippuric acid (PHA) and maleic acid doped hippuric acid (MADHA) were grown at room temperature by slow evaporation technique using dimethyl formamide (DMF) as solvent. The grown crystals were subjected to X-ray diffraction analysis which showed that both the grown crystals belong to orthorhombic structure with space group $P2_12_12_1$. The Fourier transform infrared (FTIR) spectral analysis was carried out to identify the presence of functional groups in the pure and doped crystals. The presence of hydrogen- and carbon-bonded network was studied using ^1H and ^{13}C nuclear magnetic resonance (NMR) spectral analysis. The UV-vis-NIR spectral analysis was carried out to study the optical properties of the grown crystals. It was found that the grown crystals were transparent in the entire visible region suggesting its suitability for nonlinear optical applications. The mechanical hardness of the grown crystals was studied using Vickerss micro hardness tester. The nonlinear optical (NLO) property of the grown crystals was confirmed by second harmonic generation (SHG) test.

1. INTRODUCTION

Nonlinear optics has presently established as an alternative field to electronics for the future photonic technologies. The fast growing development in optical fibre communication systems

has stimulated the search for new highly nonlinear materials capable of fast and efficient processing of optical signals. Organic nonlinear optical (NLO) materials have been intensely investigated due to their potentially high nonlinearities and rapid response in electro-optic effect compared to inorganic NLO materials [2, 3, 14]. In recent years, there has been considerable interest in the study of organic NLO crystals with good nonlinear properties because of their wide applications in the area of laser technology, optical communication, optical information processing and optical data storage technology [6]. A number of organic materials have been identified and synthesized showing considerable NLO effects. Among organic NLO materials, amino acid display specific features such as molecular chirality, absence of strongly conjugated bonds and zwitter ionic nature of the molecule [1, 13]. Hippuric acid is a colorless crystal which belongs to glycine family. It crystallizes in orthorhombic structure with space group $P2_12_12_1$ [7]. It has high transparency. The cut- off wavelength was found to be 300 nm and optical band gap 4.14eV [17, 18]. Vijayan et al. [19] have shown that the crystal grown by novel unidirectional solution growth method using dimethyl formamide (DMF) as solvent contains a low angle structural grain boundary and the SHG efficiency is found to be 1.54 times higher than that of KDP single crystal. Modified hippuric acid single crystals have been grown from aqueous solution of acetone by doping with NaCl and KCl using slow evaporation technique at constant temperature, with the vision to improve the physicochemical properties of the sample [16]. The effect of hippuric acid on different dopants has been studied and reported [8-11,15]. But the effect of hippuric acid on acid dopants and its characterization was not reported. In the present investigation, we report the effect of maleic acid on the growth and characterization of hippuric acid single crystals. The as-grown crystals were subjected to various characterization studies like X- ray diffraction (XRD), Fourier transform infrared (FTIR) spectral analysis, Nuclear magnetic resonance (NMR) spectral analysis, ultraviolet visible (UV-vis) spectroscopy, micro hardness and nonlinear optical test.

2. EXPERIMENTAL PROCEDURE

2.1. **Crystal growth.** Commercially available AR grade hippuric acid was dissolved in dimethyl formamide (DMF) with 1M concentration. The solution was continuously stirred for eight hours using a magnetic stirrer to obtain a homogenous mixture. The solution was then filtered using Whatmann filter paper to remove the suspended impurities. It was then covered using perforated cover and allowed to crystallize by slow evaporation of solvent at room temperature. Single crystals of good transparency were harvested after three months. With the same concentration of hippuric acid solution, of maleic acid was added and the same procedure was followed to get defect free single crystals of maleic acid doped hippuric acid. The as-grown crystals of pure hippuric acid (PHA) and maleic acid doped hippuric acid (MADHA) are presented in Fig.1 (a) and (b), respectively.
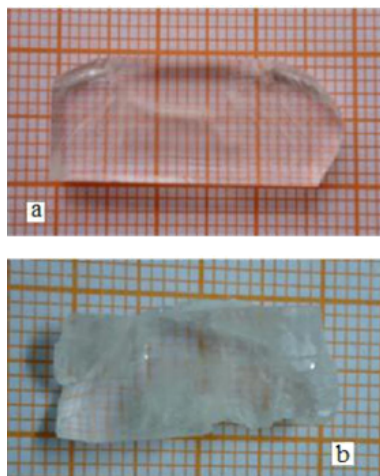
FIGURE 1. As grown crystal of PHA (a) and MADHA single crystal

3. RESULTS AND DISCUSSION

3.1. **Single crystal X-ray diffraction analysis.** The as-grown crystals of pure hippuric acid (PHA) and maleic acid doped hippuric acid (MADHA) were subjected to single crystal X-ray diffraction analysis using Enraf Nonius CAD4 X-ray diffractometer to determine the crystal structure and cell parameters. From the analysis, it was found that both the crystals belong to orthorhombic crystal system with a spacegroup $P2_12_12_1$. The unit cell parameters of PHA are in good agreement with the reported value. The calculated lattice parameter values of PHA, MADHA and the reported value are presented in Table 1 for comparison. The slight variation in the cell parameters as well as cell volume observed in the case of MADHA single crystals shows the influence of maleic acid in hippuric acid single crystals.

Data	PHA	MADHA	PHA (7)
(a)Å	8.85	8.89	8.8514
(b)Å	9.08	9.12	9.08
(c)Å	10.57	10.61	10.580
α	90	90	90
βÅ	90	90	90
γÅ	90	90	90
Space group	$P2_12_12_1$	$P2_12_12_1$	$P2_12_12_1$
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic

TABLE 1. Single crystal XRD data of PHA and MADHA

3.2. **FTIR spectral analysis.** In order to confirm the various functional groups, the as-grown crystals of PHA and MADHA were subjected to Fourier transform infrared spectral analysis.

The FTIR spectra of both the samples were recorded in the range 550-4000 cm^{-1} using Jasco-FTIR 4100/Japan spectrometer. The spectra of PHA and MADHA are shown in Fig.2 (a) and (b), respectively. In the spectrum of PHA, a sharp peak observed at 3337.21 cm^{-1} is due to N-H stretching. The presence of C-H band at 3076.87 cm^{-1} and overtones at 2000-1660 cm^{-1} support the presence of phenyl ring. The broadened envelope in the region 2500-3300 cm^{-1} is due to strongly H bonded O-H stretching of carboxylic acid. The CH stretching of CH$_2$ is observed at 2935.13 cm^{-1}. The less intense peaks in the region 2300-2700 cm^{-1} are attributed to hydrogen bonding interaction of COOH group in the crystal lattice. The peak at 1744.3 cm^{-1} is due to C=O stretching. The peaks at 1600 cm^{-1} and 1487.81 cm^{-1} are due to ring skeletal C=C bands. The peak at 1412.6 cm^{-1} is due to O-H bend. The strong peak at 1550 cm^{-1} due to NH in plane bending confirms the presence of amine group. The medium band at 1302.68 cm^{-1} arises from C-O stretching. The peak at 1174.44 cm^{-1} is due to C-N stretching. The C-H out of plane bending appears in the region 900-690 cm^{-1}. The band assignments agree with the literature data [5, 20]. In the spectrum of MADHA, the N-H stretching is observed at 3335.28 cm^{-1} and C-H stretching band is observed at 3070.12 cm^{-1}. The C=O stretching peak is observed at 1742 cm^{-1} and the C-N stretching peak is observed at 1171.54 cm^{-1}. The strong peak due to NH in plane bending is found to occur at 1548.56 cm^{-1}. The shift in the peak values is due to the incorporation of maleic acid in to hippuric acid single crystal. Moreover the intensity of transmittance has been increased for MADHA spectrum than that of PHA spectrum.
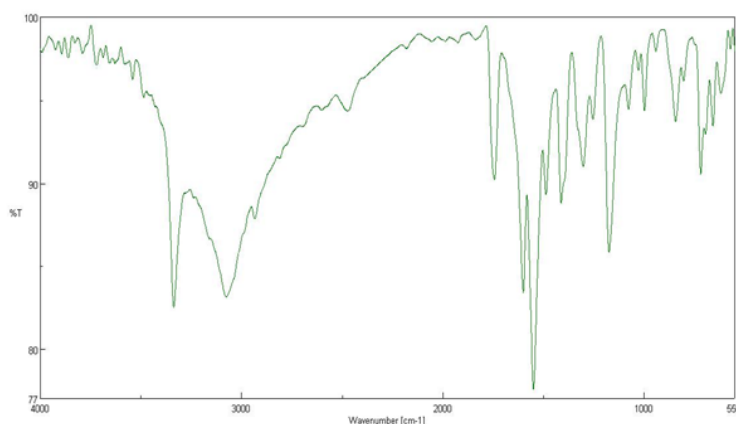

FIGURE 2. FTIR spectra of PHA single crystal

3.3. ^{1}H and ^{13}C NMR spectral analysis. In order to analyze the hydrogen- and carbon-bonded network of PHA and MADHA single crystal, ^{1}H and ^{13}C NMR spectra were recorded using a Bruker 300 MHz spectrometer with deuterated DMSO as solvent. The ^{1}H NMR spectra of both PHA and MADHA single crystals are shown in Fig.3 (a) and (b), respectively. In the ^{1}H NMR spectrum of PHA, the peak at 12.65 ppm equivalent to ^{3}H obviously indicates the presence of COOH group. The singlet at 8.85 ppm equivalent to ^{1}H arises due to NH proton.
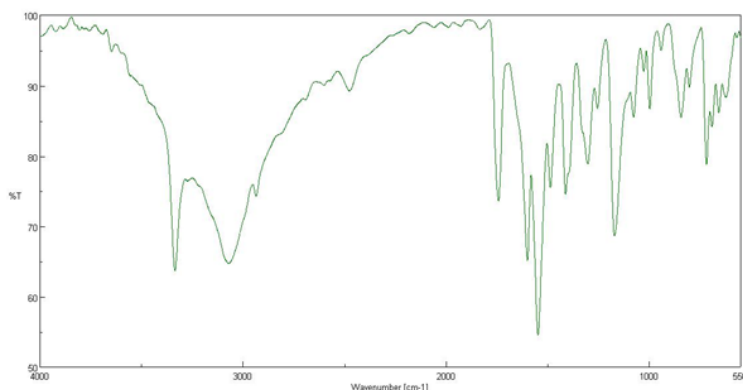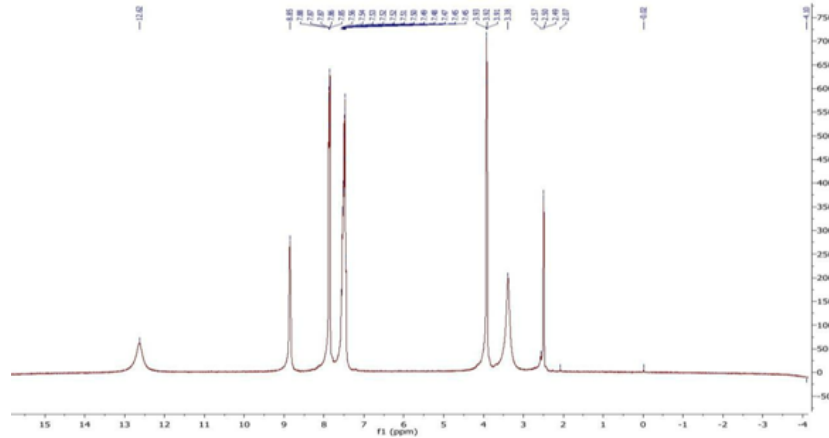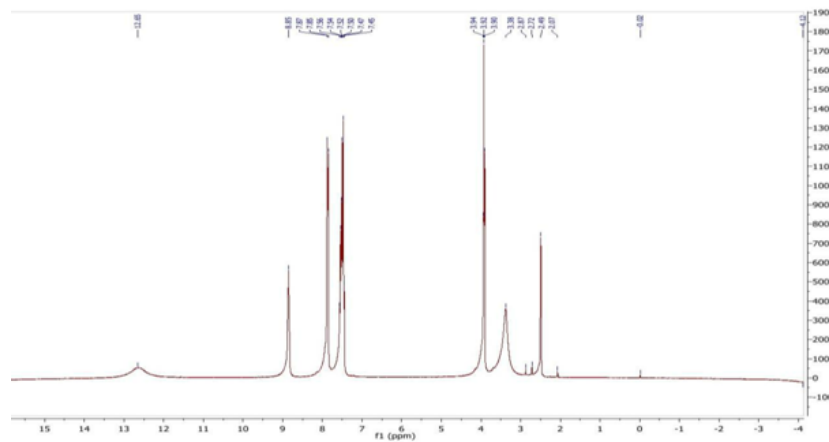
FIGURE 3. FTIR spectra of MDHA single crystal

The presence of an aromatic ring equivalent to 5H is indicated by the multiplet between 7.45 and 7.87 ppm. The peak at 2.49 ppm equivalent to 2H indicates the presence of CH_2 group. The peak centered at 3.92 ppm is due to the solvent DMSO. The broad signal at 3.38 ppm is due to the traces of water in DMSO.The spectrum of MADHA shows number of peaks in the aromatic region which is due to the doping of maleic acid into the pure hippuric acid crystal. Moreover variation in the peak intensities observed in the spectrum of MADHA single crystal shows the influence of maleic acid in hippuric acid single crystals. The ^{13}C NMR spectra of both PHA and MADHA single crystals are shown in Fig.4 (a) and (b), respectively. In the ^{13}C NMR spectrum of PHA, the most deshielded carbon appears at 172.22 ppm which is due to COOH. The peak at 167.39 ppm is attributed to carbonyl carbon which appears as a singlet in the spectrum. The presence of signal at 134.66, 132.28, 129.21 and 128.08 ppm indicates the aromatic carbon. The singlet at 42.10 ppm is attributed to the carbon of CH2. The signal at 40.25 ppm is due to the solvent DMSO. In the ^{13}C NMR spectrum of MADHA, the COOH carbon appears at 176.99 ppm, carbonyl carbon at 172.15 ppm, and the aromatic carbons at 139.43, 137.04, 133.96 and 132.84. The variation observed in the spectra of MADHA single crystal confirms the incorporation of maleic acid into hippuric acid crystal.

3.4. **UV-Vis NIR spectral analysis.** The optical absorption of the crystal is an important factor for analyzing the second harmonic generation property. In UVvisible studies, electrons in $\pi$and σ orbitals get excited from the ground state to excited energy states on absorbing UV and visible light and hence provide important structural information [4]. Hence the as-grown crystals of PHA and MADHA were subjected to UV-vis-NIR absorption studies using UV-vis spectrophotometer, Systronics 2202 in the range 200-1100 nm. The spectra obtained for both the crystals are shown in Fig.5. It is seen from the absorption spectrum that both the crystals are transparent in the entire visible range without any absorption peak which is an essential parameter for NLO crystals. The absence of absorption of light in the visible region is an intrinsic property of all amino acids. The lower cut-off wavelength of PHA single crystal was found to be 280 nm and

FIGURE 4. ^{1}H NMR spectra of PHA single crystal

FIGURE 5. ^{1}H NMR spectra of MADHA single crystal.

that of MADHA single crystal was found to be 287 nm. The transmission window in the visible region enables good optical transmission of the second harmonic frequencies of Nd: YAG laser.

3.5. Micro hardness studies.

Micro hardness measurements for the grown crystals of PHA and MADHA were carried out using Leitz Weitzler hardness tester fitted with a diamond pyramidal intender attached to an incident light microscope. The well polished crystals were placed on the platform of the Vickerss hardness tester and three loads were applied over a fixed interval of time. The indentation time was kept as 5s for all the loads. The lengths of the two diagonals were measured and the average of the diagonals (d) was calculated. The hardness Hv of the crystal was calculated by the relation $H_v = 1.8554$ P/d^2 Kg/ mm^2

where P is the applied load and d is the mean diagonal length of the indenter impression. Variation of hardness number with applied load for both PHA and MADHA single crystals are
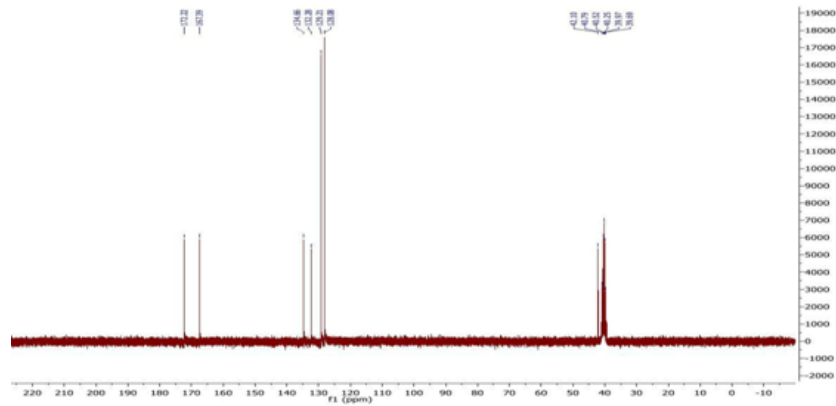
FIGURE 6. ^{13}C NMR spectra of PHA single crystal
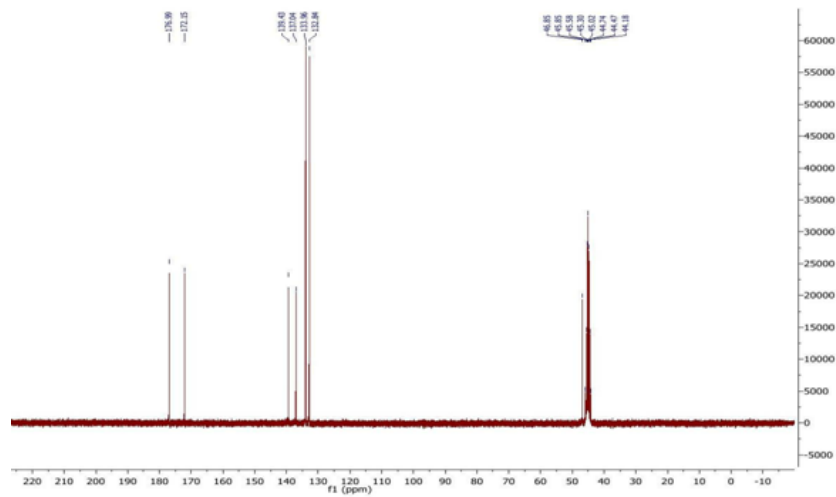
FIGURE 7. ^{13}C NMR spectra of MADHA single crystal.

shown in Fig.6. It is seen from the figure that the hardness increases as the load is increased. The hardness value of MADHA single crystal was found to be 57.9kg/mm^2 and that of PHA single crystal was found to be 53.2kg/mm^2. The hardness value of MADHA single crystal is found to be more than that of PHA single crystal.

3.6. **Nonlinear optical test.** In order to confirm the NLO property, the grown crystals were subjected to a second harmonic test using Kurtz and Perry powder technique [12]. A Q-switched Nd-YAG laser beam of wavelength 1064 nm with a pulse rate of 8ns was used. An input pulse of 1.1 mJ/pulse was supplied. The grown crystals were powdered with a uniform particle size and placed in a micro capillary tube of uniform bore and exposed to laser radiations. The second harmonic radiation generated by the randomly oriented micro crystals was focused by a lens and detected by a photo multiplier tube. Potassium dihydrogen phosphate (KDP) was taken as
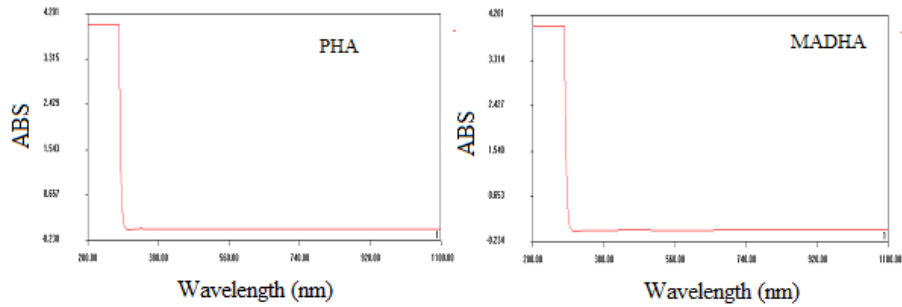
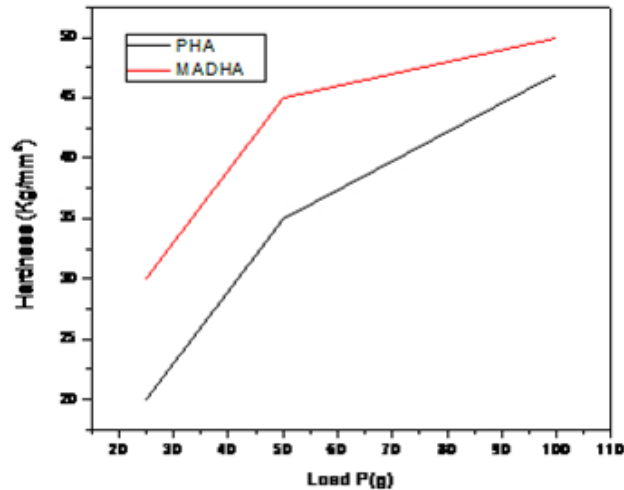FIGURE 8. UV-vis-NIR spectra of both PHA and MADHA single crystals

FIGURE 9. Variation of hardness number with load for PHA and MADHA single crystals

reference material. The second harmonic generation was confirmed by the green emission of wavelength 532 nm from both the samples. The output of PHA single crystal was found to be 148 mV and that of MADHA single crystal yielded an output of 152 mV. The same procedure was adopted for KDP crystal which gives an output of 120 mV. The result obtained shows that the SHG efficiency of pure and doped samples is 1.233 and 1.266 times greater than that of KDP. Also it is found that the doped one has more efficiency than the pure one. This observed SHG property suggests the suitability of the material for NLO device applications.

4. Conclusion

Transparent single crystals of PHA and MADHA are successfully grown at room temperature by slow evaporation technique using DMF as solvent. The XRD analysis revealed that both the grown crystals belong to orthorhombic crystal system with space group $P2_12_12_1$. However there is a slight increase in the lattice parameters and volume of MADHA crystal. The presence of functional group was confirmed by FTIR spectral analysis. The carbon- hydrogen bonded network has been confirmed by ^{1}H and ^{13}C NMR spectral analyses. The UV-vis-NIR spectral analysis showed a wide transparency in the entire visible region and suggests its suitability for NLO applications. The cut-off wavelength of PHA and MADHA crystals are found to be 280 and 287 nm respectively. The micro hardness studies revealed that the hardness number of both the crystals increases with increasing load, and the hardness number of MADHA was found to be greater than that of PHA single crystal. The NLO test showed that the SHG efficiency of both the crystals is greater than KDP and the doped crystal is found to be more efficient than the pure one. The good optical properties and SHG efficiency make both the crystals a potential candidate for photonic device fabrication.

Acknowledgments

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