Growth and Characterization Studies: Potential Nonlinear Optical Single Crystals Hippuric Acid (HA)

A. Kumaresh, R. Arun Kumar*

GRD Centre for Materials Research, PSG College of Technology, Coimbatore, India

*Corresponding author: rarunpsgtech@yahoo.com

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Abstract Organic non-linear optical materials receive much attention owing to their very large second order nonlinearities, ultra-fast response times and high optical damage thresholds. In the present work, low temperature solution growth technique has been employed to grow non-linear optical hippuric acid (HA) $C_6H_5CONHCH_2COOH$ single crystal with dimensions $10 \times 6 \times 3 \text{ mm}^3$ were obtained in a period of 18 days using acetone as solvent. Powder XRD analysis reveals that the crystal belongs to an orthorhombic system with space group $P2_12_12_1$ and lattice parameters were found to be $a = 8.8514 \text{ \AA}$, $b = 9.0842 \text{ \AA}$, $c = 10.5807 \text{ \AA}$. UV optical absorption analysis on these samples reveals the transparency of the crystal in the visible region. The bonding structure and molecular associations due to chemical reactions were analyzed by FTIR spectroscopy.

Keywords Growth from Solution, NLO Property, SHG, Powder XRD, UV-Vis-NIR, FTIR

1. Introduction

Coherent radiation from common lasers can be converted to any other desirable wavelengths using nonlinear optical (NLO) effects by means of NLO crystals. Electronic and photonic materials are the key elements for the scientific growth and technological advances in new millennium. The nonlinear optical (NLO) organic materials have been the subject of extensive theoretical and experimental investigations during the past two decades [1-2].

Nonlinear optics (NLO) has wide applications in the field of telecommunication and information devices [3-6]. Nonlinear optics is playing a major role in the emerging photonics and optoelectronics technologies. New non linear optical frequency conversion materials have a significant impact on laser technology, optical communication and optical data storage [7-9]. Organic NLO materials are attracting a great deal of attention for possible use in optical devices because of their large optical non linearity, low cutoff wavelength, short response time and high threshold

for laser power [10-12].

Recent interest in quantum electronics has centered on finding a new materials for efficient second harmonic electro optic modulation [13]. The organic NLO material contains an optically active atom i.e. it will have hyper polar molecule, which favors the formation of big size crystals [14]. Hippuric acid (HA) with molecular formula $C_6H_5 - CO - NH - CH_2 - COOH$ is also referred as benzamino acetic acid is an organic nonlinear material. It is formed in the order of orthorhombic structure. It is an excellent crystal for second harmonic generation because of its high conversion efficiency [15]. In the present work, investigation with various solvents have been taken for the growths of hippuric acid single crystal and found that, defect-free crystals of HA can be grown using acetone as a solvent.

2. Single Crystal Growth

Low temperature solution growth technique has been employed to grow HA single crystal using acetone as solvent. The analytical grade HA was taken and dissolved in acetone to prepare the saturated solution. The saturated solution of HA was obtained by dissolving the material with continuous stirring of solution using magnetic stirrer. The resulting solution was filtered using borosil filter paper of porosity $0.1 \mu\text{m}$. The filtered solution was allowed to evaporate in a petri dish at ambient temperature. High quality transparent colourless crystals of size $10 \times 6 \times 3 \text{ mm}^3$ were obtained in a period of 18 days. Its structural formula and molecular structure are shown in Fig 1&2 respectively. Its crystal structure projected along the a-axis is shown in Fig 3 and the photograph of grown HA crystal is as shown in Fig 4.

Figure 1. Structural formula of HA

Figure 2. Molecular structure of HA

Figure 3. Crystal structure of HA projected along the a-axis

Figure 4. Photograph of HAADP single crystal

3. Crystal Characterizations

3.1. Powder XRD Analysis

The grown crystals of HA was powdered and subjected to X-ray diffraction analysis using STOE powder diffraction system loaded in Si-911 loader. The wavelength of X-ray radiation is $1.5406 \text{ \AA}$. The anode voltage was 35 kV with a current of 30 mA. The range of 2θ was scanned from 10° - 70° . Intensity versus 2θ was recorded for HA and shown in

Fig 5. From the powder X-ray diffraction data, the lattice parameters and the cell volume have been calculated using XRDA software package. It has been found that the crystal belongs to the orthorhombic system with space group $P2_12_12_1$ and lattice parameters $a = 8.8514 \text{ \AA}$, $b = 9.0842 \text{ \AA}$, $c = 10.5807 \text{ \AA}$. The crystallography data is given in table 1.

Figure 5. Powder XRD spectrum of HA crystal

3.2. UV-Vis-NIR Analysis

The grown crystal of HA was subjected to UV-Vis-NIR spectral analysis. A crystal of thickness 3 mm was used to record the spectrum in the wavelength range between 200 - 1000 nm using Varian Cary 5E UV-Vis-NIR spectrometer. The UV absorption spectrum of HA is shown in Fig 7. It reveals that the HA crystal has wider transparency range extending into entire visible and IR region. It is evident that crystal has absorption around 300 nm, which is may be assigned to electronic transition in the aromatic ring C=O groups [5]. The cutoff wavelength around 300 nm is sufficiently good for second harmonic generation and other applications in the blue region [10].

3.3. FTIR Analysis

FTIR spectrum was taken from the synthesized sample by pelletizing them with spectroscopic KBr from Merck by applying a pressure of 370 MPa. The pressure was given through hydraulic press. The FTIR spectrum of HA is recorded in the range from 400 to 4000 cm^{-1} using KBr pellet technique by Bruker IFS 66v FTIR spectrometer. The spectrum obtained is shown in Fig 6. The characteristic absorption of HA and bond assignment of functional groups present in the grown crystal are given in the table 2.

4. Conclusions

Optically good quality of nonlinear optical hippuric acid single crystals was grown by solution growth technique. The X-ray diffraction study revealed that the grown crystal

belongs to orthorhombic system. FTIR analysis confirms the functional groups present in the crystal. The optical absorption analysis revealed that Hippuric acid crystals have a UV cutoff wavelength around 300 nm and has wider

transparency range extending into entire visible and IR region. From this optical assessment we found that it has large transmission range and it may be used for frequency doubling and other optical application.

Table 1. Unit cell parameters of HA crystal

Sample	Lattice parameters			$\alpha=\beta=\gamma$ (°)	Structure	Space group
	a (Å)	b (Å)	c (Å)			
HA	8.8514	9.0842	10.5807	90	Orthorhombic	P2 ₁ 2 ₁ 2 ₁

Figure 6. UV visible spectrum of HA

Figure 7. FTIR spectrum of HA crystal

Table 2. Characteristic absorption and bond assignment

Characteristic absorption of HA (cm ⁻¹)	Bond assignments
3341 cm ⁻¹	N - H deformation
3073 cm ⁻¹	Hydrogen bonded OH stretching
2938 cm ⁻¹	CH stretching of CH ₂
1988 cm ⁻¹	N - H stretching
1744 cm ⁻¹	C = O stretching
1600 cm ⁻¹	C = O stretching of COOH group
1465 cm ⁻¹	C-C stretching
1335 cm ⁻¹	C - N stretching
629 cm ⁻¹	C - H deformation

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