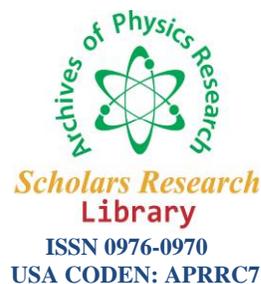




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## Crystal Growth, Optical and Structural Properties of MNA Doped L-Histidine Single Crystal

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### ABSTRACT

New organic non-linear optical (NLO) material L-histidine Meta nitro aniline (LH-mNA) has been grown by slow evaporation solution growth technique at 450C temperature. High optical quality and appropriate size of crystals were grown under optimized growth conditions. The grown crystals were yellowish color and transparent. UV-Visible transmission spectrum shows 99% transmission of light in the entire visible region and cut-off wavelength was occurs at 268 nm. The optical band gap was calculated to be 4.62 eV. With the help of optical data to be calculate absorption coefficient ( $\alpha$ ), extinction coefficient ( $k$ ), refractive index ( $n$ ), dielectric constant ( $\epsilon$ ), optical conductivity ( $\sigma_{op}$ ). Photoluminescence study provides information of discrete levels of energy states, which is show that material emits the different colors of wavelength in different regions. The crystalline nature of grown crystal was confirmed by powder X-ray diffraction analysis (XRD). Scherer formula calculates particle size and lattice strain. With the help of XRD data make the W-H plot, which is provide particle size and lattice strain.

**Keywords:** Non-linear optical, Solution growth, UV-Visible Spectroscopy, Refractive index, Dielectric constant, Optical conductivity, Powder X-ray diffraction analysis.

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### INTRODUCTION

The research of new materials is backbone of the solid-state physics they are mostly discovered by crystal researchers who are crystal growers. Solid state physics provided a basis for the expansion of knowledge for developing the methods to grow naturally occurring crystals in laboratory. The research on new organic nonlinear optical (NLO) materials have attracted due to their unique properties such as high speed information processing, frequency conversion, optical switching. Organic nonlinear compounds have large macroscopic second –order NLO susceptibilities  $\chi_2$  which makes differs organic material to inorganic materials [1-4]. To increase the second-order NLO property mixed to organic nonlinear material. Amino acids are good materials for optical second harmonic generation (SHG) as they contain zwitterions, which create the hydrogen bonds used for the generation of non-centrosymmetric structures favourable for attractive SHG properties of the crystal.

In this paper, we reported the L-Histidine Meta nitro aniline. Amino acids combine many of the properties and reactions of both amine and carboxylic acids. Actual structure of amino acid is ionic and depends on the Ph value.

The carbonyl group (COOH) loses a proton, giving a carboxyl-ate ion, and amino group is protonated to an ammonium ion. This structure is called a dipolar ion or Zwitterions. The basic structure of organic nonlinear optical (NLO) materials is based on the  $\pi$  bond system. Due to the overlap of  $\pi$  orbital, delocalization of electronic charge distribution leads to a high mobility of the e- density. L-Histidine belongs to amino acid group and mNA belongs to aniline group, which shows the good second harmonic generation property. Hence in the present investigation reported the bulk crystal growth of LH-mNA compound. The grown crystals were subjected to different characterization powder XRD, particle size, lattice strain, W-H plot, UV-visible transmission, refractive index, absorption coefficient, extinction coefficient, dielectric constant, optical conductivity, band gap, PL study, SHG.

## EXPERIMENTAL

### Material synthesis

L-Histidine and Meta nitro-aniline were mixed in the stoichiometric ratio of 1:1 in water acetone mixture because MNA is less soluble in water. The mixture was placed in a magnetic stirrer for 5-6 hours. After repeated crystallization, saturated solution was prepared at 45°C using the synthesized salts [5]. The solution was finally filtered twice using micro- what mann filter papers to eliminate unwanted impurities. The filtered solution was kept in a covered with a perforated sheet and placed in a dust free atmosphere. A good quality of single crystal of optimum size was obtained with in a period of 6 weeks at room temperature (32°C). The photograph of as grown crystal of L-Histidine meta nitro-aniline (LH-mNA) is shown in figure (1).



Figure 1: This Photograph of as grown crystal of LH-mNA

### Characterizations

In this paper, we try to grow the crystal of LH-mNA by slow evaporation method. Different characterization characterized the grown crystals such as UV-Visible Spectroscopy and Photoluminescence Spectroscopy, and Powder XRD analysis. From the UV, optical data were calculated to be optical band gap, absorption coefficient ( $\alpha$ ), extinction coefficient ( $k$ ), refractive index ( $n$ ), dielectric constant ( $\epsilon$ ), optical conductivity ( $\sigma$ ). From the XRD data were calculated to be crystal size, lattice strain, full width half maxima, and W-H plot.

## RESULTS AND DISCUSSION

### UV-VIS Spectral Studies

UV-Visible spectroscopy determines the Linear optical property. The interaction of UV and Visible radiation with matter can provide qualitative information's of compound. The wavelength range of UV-radiation starts from 200 to 400 nm. Visible light, consider being 400 to 800 nm. Chromophores molecular groups are absorbed visible or UV radiations. For  $\pi\text{-}\pi^*$  transition to occur, a molecule must possess a chromophore with an unsaturated bond, such as C=C, C=O, C=N and so on. The other transition ( $n\text{-}\pi^*$ ) that only occurs in the UV/VIS region. So, we can say that organic molecules are contains atoms with non-bonded electrons like N2, O2, S and H2 atoms. UV-VIS spectrum analysis has been carried out using shimadzu spectrophotometer in the wavelength range of 200-800 nm [6]. Transmission, absorption, and reflectance spectra are shown in figure (2). From the spectra, it is seen that the cut-off wavelength is found 268 nm. Transmission is observed up to 99% and absorption is almost 0%. Transmission is constant in the entire visible region clearly shows that the crystal possesses good optical transparency for the second harmonic generation. From the UV-optical data we are calculated absorption coefficient ( $\alpha$ ), excitation coefficient (k), refractive index (n), and optical band gap ( $E_g$ ).

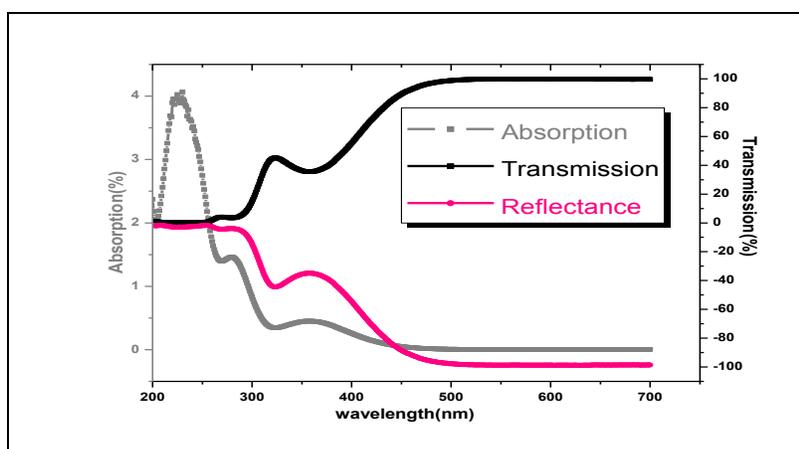


Figure 2: This Photograph of as grown crystal of LH-mNA

### Determination of Optical Constant

The optical behaviors of materials are imperative to determine its applications in photonics devices. To acquaintance of optical constants of a material such as optical band gap, refractive index (n), absorption coefficient ( $\alpha$ ), excitation coefficient (k), dielectric constant ( $\epsilon$ ), optical conductivity ( $\sigma_{OP}$ ), band gap ( $E_g$ ) are quite essential to study the materials potential opto-electronic applications [7-8].

The absorption coefficient ( $\alpha$ ) for the grown crystal can be determined using formula-

$$\alpha = 2.303 * \log (1/T) / d \dots\dots\dots (1)$$

Where 'T' is transmittance and 'd' the thickness of the crystal. Due to the direct band gap, the crystal under study has an absorption coefficient ( $\alpha$ ) obeying the following relation-

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

Where ‘A’ is constant, ‘Eg’ optical band gap, h is plank constant, ‘ν’ is frequency of incident photons. The band gap of grown LHMNA crystal was estimated by plotting  $(\alpha h\nu)^2$  versus  $h\nu$ . Band gap is shown in figure 3(a).

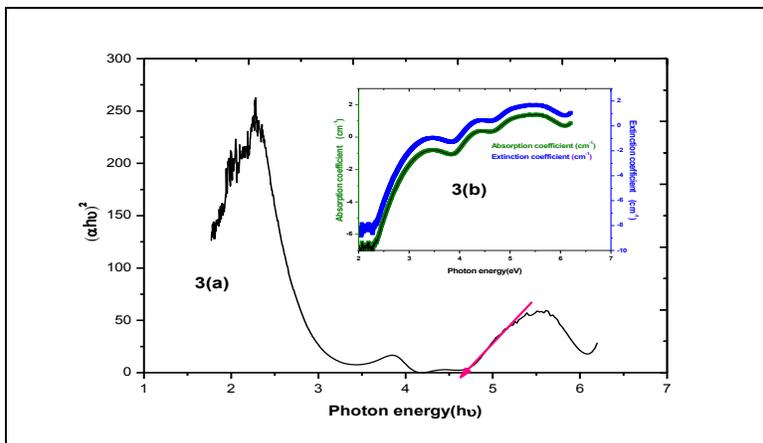


Figure 3 (a, b): Optical band gap, absorption, and extinction coefficient of grown crystal LH-mNA

The band gap energy of grown crystal was found to be 4.62 eV. The extinction coefficient (k) can be determined using formula-

$$K = \alpha \lambda / 4\pi \dots\dots\dots (3)$$

The plot of absorption coefficient, extinction coefficient versus photon energy (eV) is shown in figure 3(b). From the figure, absorption coefficient depended on photon energy. It is evidence that the absorption coefficient varies from (-1.09 to 0.821 cm<sup>-1</sup>) with increasing photon energy (3.82 to 6.21 eV). In other words, we can say that in UV region (200-350 nm) absorption coefficient is high and in visible region (400-700 nm) crystal show transparency which is applicable for optoelectronic devices.

Extinction coefficient (K) also varies (-0.26 to 1.48 cm<sup>-1</sup>) with photon energy (3.75 to 6.20 eV). The variation in value of excitation coefficient is due to the variation in the absorbance. In UV region (200 to 350 nm) excitation coefficient is maximum and in visible region (400 to 700 nm) almost transparent nature of the crystal.

**Refractive Index (n) and Dielectric Constant**

In many instances researches, the optical constants were measure by examining the transmission through a transparent crystal substrate. The amount of light that transmitted through the crystal depends on the amount of the reflection and absorption that takes place along the light path. The refractive index n was determined from a transmittance spectrum as a function of the photon energy within the wavelength in the range 300-700 nm [9].

The reflectance (R) is derived from the relation-

$$R = \sqrt{1 \pm (1 - \exp(-\alpha t) + \exp(\alpha t) / 1 + \exp(-\alpha t)) \dots\dots\dots (4)}$$

From the above equation, refractive index can be calculated by following relation-

$$n = 1 + \sqrt{R} / 1 - \sqrt{R} \dots\dots\dots (5)$$

The graph of refractive index is show in figure 4(a). From the graph, it is observed that refractive index (n) decreases with increases wavelength. In the UV region, refractive index (n) is varies from 3 to 1.32 at wavelength 265 to 350 nm. and gets saturated beyond the wavelength of 400 to 700 nm. The refractive index of grown LH-mNA crystal for longer wavelength (visible region) was calculated to be 1.300. Variations in the values of refractive index are showing that different electronic transition in different energy states of compound.

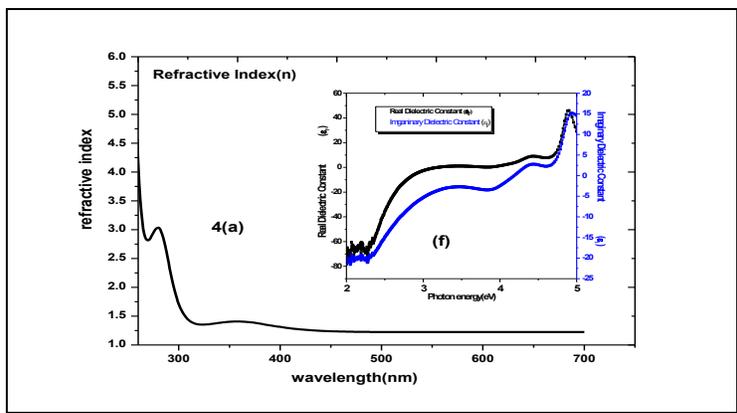


Figure 4(a, b): Refractive index and dielectric constant of grown crystal LH-mNA

The real and imaginary parts of the dielectric function are related by the Kramers-Kronig relations. The real and imaginary parts of dielectric constant ( $\epsilon_r$ ,  $\epsilon_i$ ) were calculated by using equations (6-a, 6-b).

$$\epsilon_r = n^2 - k^2 \dots\dots\dots (6a)$$

$$\epsilon_i = 2 n k \dots\dots\dots (6b)$$

The real and imaginary parts of the dielectric constant of the grown crystal were determined and shown in figure 4(b). From the graph, both real and imaginary part of dielectric constant increases with increase of photon energy. Both dielectric constants are maximum at 4.8 eV photon energy. The real part of the dielectric constant increases linearly with higher value than the imaginary part. The lower value of dielectric constant with wide band gap of LH-mNA crystal suggests the suitability of optoelectronic devices.

**Optical Conductivity ( $\sigma_{op}$ )**

The optical conductivity is a measure of the frequency response of the material when irradiate with light, calculated by following relation-

$$\sigma_{op} = \alpha n c / 4\pi \dots\dots\dots (7)$$

Where c is velocity of light. Figure (5) shows the variation of optical conductivity with the incident photon energy. Optical conductivity show that material is useful in optical devices, photonics devices etc.

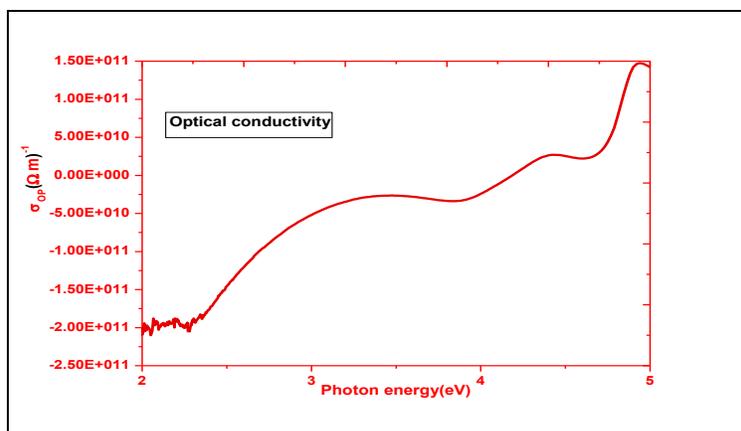


Figure 5: Optical conductivity of grown crystal LH-mNA

### Photoluminescence Spectral Study

Organic materials have very broad spectra of excitation and emission with well identify bands. PL of LH-mNA crystal provides information of different energy states available between valence band and conduction band responsible for radiative recombination. PL is occurring when electron is excited to the conduction band and after 10-8 sec. gets return to the ground state by emission of radiation in the form of photon. A PL spectrum of LH-mNA is shown in figure (6). From the figure, there are two sharp peaks at 450 nm and 487 nm. In the graph 450 nm is excitation wavelength in far UV region at which electron get raised to excited state. In this region colour of wavelength is violet or indigo. In visible region 487 nm is emission wavelength of PL spectra, at this wavelength electrons get down to the ground state in the form of emission of the light in blue and aqua colors. In the spectrum, some small peaks are present in the far visible regions that are at 510 nm, 517 nm, 585 nm, 594 nm. These peaks are emitted green, yellow and orange colors of wavelength. Beyond 600 to 900 nm spectrum is wide transparent in nature. The emission of green light is proof that grown crystal of LH-mNA applicable for second harmonic generation devices.

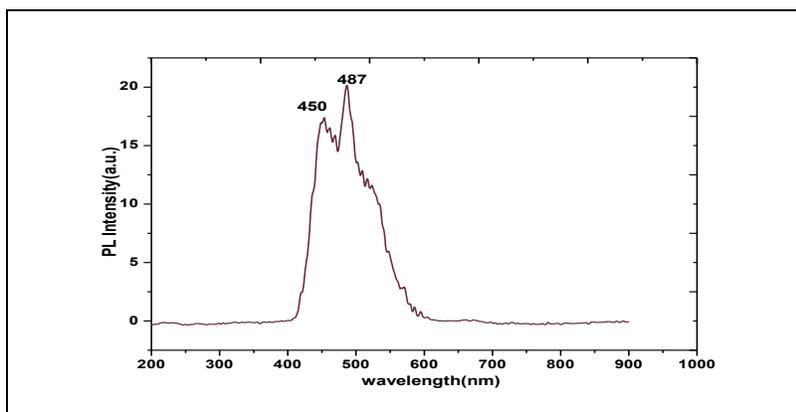


Figure 6: Photoluminescence of as grown crystal of LH-mNA

### Powder XRD Analysis

Powder X-ray diffraction was carried out using a X-ray diffractometer with Cu K $\alpha$  ( $\lambda = 1.5405 \text{ \AA}$ ) radiation. The sample was scanned over the range  $10^\circ$ – $60^\circ$  at a rate of  $1^\circ/\text{min}$ . The X-ray diffraction pattern of LH-mNA is shown in figure 7(a). X-ray diffraction is an important technique to obtain structural information on an atomic scale from both crystalline and non-crystalline (amorphous) materials [10-15]. The powder diffraction data of grown crystal is shown in table (1).

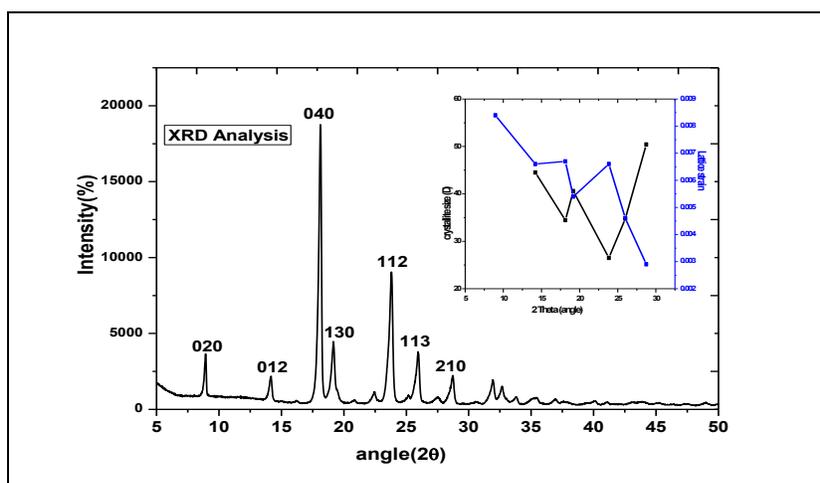


Figure 7(a, b): XRD analysis, crystal size and lattice strain of as grown crystal of LH-mNA

The Scherrer's formula is used for the determination of grain size from broadened peaks. The formula is not expected to be valid for very small grain size ( $< 10 \text{ nm}$ ). Particle size of grown crystal was calculated by Scherrer's formula-

$$\beta = k \lambda / D \cdot \cos(\theta) \dots\dots\dots (8a)$$

Where  $\beta$  – peak width in radians,  $\lambda = 1.540 \text{ \AA}$  wavelength,  $D =$  grain size,  $k =$  constant (0.9 to 1 depending upon grain shape). The average particle size of grown crystal is  $40.90 \text{ nm}$ .

The lattice strain occurs due to the displacements of the unit cells about their normal positions. The lattice strain of grown crystal was calculated by following relations-

$$\beta (2\theta) = \eta \tan(\theta) \dots\dots\dots (8b)$$

where  $\eta$  is lattice strain of crystal. The crystal size and lattice strain graph in figure 7(b). From the figure, particle size varies with the angle  $2\theta$ .

Table 1: XRD data of LH-mNA crystal

2θ	Height (cst)	Rel. Int. (%)	d spacing (Å)	FWHM (red.)	Crystallite size (nm)	Lattice strain
8.953	3593	18.4	9.914	0.00264	55.14	0.0084
14.187	2182	11.7	6.260	0.00328	44.5	0.0066
18.14	18682	100	4.894	0.00424	34.47	0.0067
19.17	4374	23.9	4.630	0.00362	40.58	0.0054
23.82	9035	49.5	3.734	0.00559	26.5	0.0066
25.99	3660	20.6	3.431	0.00428	34.76	0.0046
28.76	2026	12.1	3.108	0.00297	50.41	0.0029

Particle size is maximum at 28.80 angle. The lattice strain decrease with increase crystallite size of the sample. The average lattice strain is calculated to be 0.0058. From the W-H method crystal size and lattice strain were calculated. Strain and particle size are calculated from the slope and y- intercept of the fitted line respectively. From the W-H plot crystallite size and lattice strain were calculated to be 53.3 nm, 0.00164 respectively. W-H plot is show in figure (8).

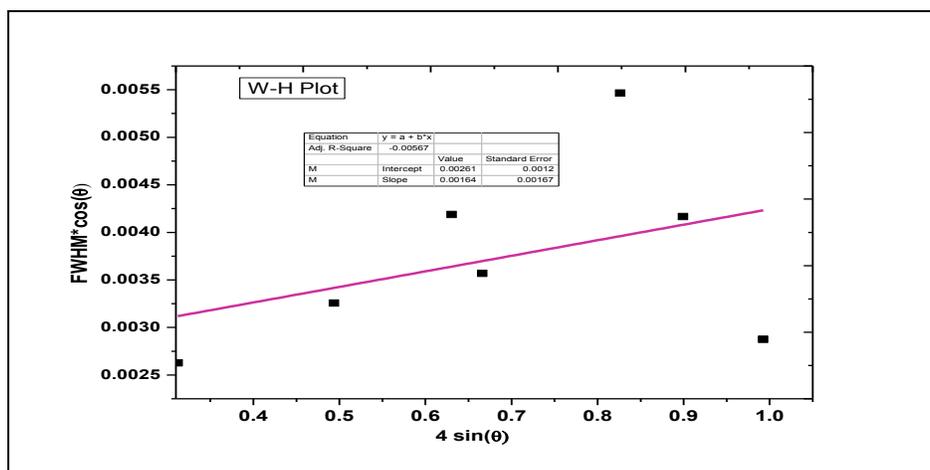


Figure 8: W-H plot of LH-mNA crystal

## CONCLUSION

The single crystal of organic compound LH-mNA was grown by slow evaporation techniques at 45°C temperature using distilled water as a solvent. Crystals are pure transparent. Crystal show good transparency in the entire UV-visible region, thus confirming the suitable for SHG. Optical bang of crystal is observed 4.62 eV. Extinction coefficient, refractive index (n), dielectric constant ( $\epsilon$ ), optical conductivity properties shows all favorable conditions

for photonic devices. X-ray diffraction peaks indicates that the crystal is perfectly crystalline in nature. PL spectrum reveal that very broad excitation and emission spectra of grown crystal.

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